OCT 17 1924

JOURNAL

OF

THE CHEMICAL SOCIETY

CONTAINING

PAPERS COMMUNICATED TO THE SOCIETY

1924, VOL. 125, SEPTEMBER

President:

W. P. Wynne, D.Sc., F.R.S.

Vice-Presidents

WHO HAVE FILLED THE OFFICE OF PRESIDENT:

H. B. Dixon, C.B.E., D.Sc., F.R.S.
P. F. Frankland, C.B.E., LL.D., F.R.S.
W. H. Perkin, Sc.D., LL.D., F.R.S.
Sir W. J. Pope, K.B.E., LL.D., F.R.S.
Sir James Walker, LL.D., F.R.S.

Vice-Presidents:

E. C. C. Baly, C.B.E., F.R.S.
A. J. Greenaway, F.I.C.
J. T. Hewitt, D.Sc., F.R.S.
G. T. Morgan, O.B.E., D.Sc., F.R.S.
James C. Philip, O.B.E., D.Sc., F.R.S.
J. M. Thomson, LL.D., F.R.S.

Treasurer:

J. F. Thorpe, C.B.E., D.Sc., F.R.S.

Secretaries:

T. Slater Price, O.B.E., D.Sc., Ph.D., F.R.S.
C. S. Gibson, O.B.E., M.A., M.Sc.

Foreign Secretary:

Arthur W. Crossley, C.M.G., C.B.E., F.R.S.

Ordinary Members of Council:

E. F. Armstrong, D.Sc., F.R.S.
D. R. Boyd, D.Sc., Ph.D.
O. L. Brady, D.Sc., B.A.
C. Dorée, D.Sc.
A. E. Dunstan, D.Sc.
J. J. Fox, O.B.E., D.Sc.
W. N. Haworth, D.Sc.
I. M. Heilbron, D.S.O., D.Sc.
C. K. Ingold, D.Sc., F.R.S.
B. Lambert, M.A.
J. W. McBain, Ph.D., F.R.S.
H. McCombie, D.S.O., M.C., D.Sc.
W. H. Mills, Sc.D., F.R.S.
G. W. Monier-Williams, O.B.E. M.C., Ph.D.
T. S. Moore, M.A., B.Sc.
J. R. Partington, M.B.E., D.Sc.
F. L. Pyman, D.Sc., Ph.D., F.R.S.
J. Reilly, D.Sc., D.ès-Sc.

Assistant Secretary:

S. E. Carr.

Librarian:

F. W. Clifford.

Burlington House, London, W. 1

Telephone—Gerrard 6322.

LONDON: GURNEY AND JACKSON

33, PATERNOSTER ROW, E.C. 4

Printed in Great Britain by Richard Clay & Sons, Ltd., Bungay, Suffolk.

Committee of Publication:

H. B. Baker, C.B.E., D.Sc., F.R.S.
E. C. C. Baly, C.B.E., F.R.S.
H. Bassett, D.Sc., Ph.D.
O. L. Brady, D.Sc.
A. W. Crossley, C.M.G., D.Sc., F.R.S.
H. W. Dudley, O.B.E., Ph.D.
U. R. Evans, M.A.
J. J. Fox, O.B.E., D.Sc.
C. S. Gibson, O.B.E., M.A.
W. N. Haworth, D.Sc., Ph.D.
I. M. Heilbron, D.S.O., D.Sc.
T. A. Henry, D.Sc.
T. M. Lowry, C.B.E., D.Sc. F.R.S.
J. W. McBain, Ph.D., F.R.S.
H. McCombie, D.S.O., M.C., D.Sc.
J. I. O. Masson, M.B.E., D.Sc.
W. H. Mills, Sc.D., F.R.S.
T. S. Moore, M.A., B.Sc.
G. T. Morgan, O.B.E., D.Sc., F.R.S.
J. C. Philip, O.B.E., D.Sc., F.R.S.
R. H. Pickard, D.Sc., F.R.S.
T. S. Price, O.B.E., D.Sc., F.R.S.
F. L. Pyman, D.Sc., F.R.S.
N. V. Sidgwick, Sc.D., F.R.S.
J. F. Thorpe, C.B.E., D.Sc., F.R.S.
W. P. Wynne, D.Sc., F.R.S.

Editor:
Clarence Smith, D.Sc.

Indexer:
Margaret Le Pla, B.Sc.

INFORMATION FOR CANDIDATES FOR FELLOWSHIP

The Chemical Society, founded in 1841 and first granted a Royal Charter in 1848, now numbers some 4,000 Fellows. Each Fellow is entitled to receive one copy of the Journal and of such other publications of the Society as the Council may determine, to use the Library, either directly or through the post, and to take part in the meetings of the Society. Experimental work is assisted by grants from the Research Fund. Fellows are also allowed certain privileges by kindred societies.

The publications include the *Journal*, containing papers communicated to the Society, the *Abstracts*, covering the current literature in pure Chemistry, the *Indexes*, and the *Annual Reports* on the progress of Chemistry.

The *Library* contains 27,575 books and 302 current journals, covering applied as well as pure chemistry.

The *Meetings*, including those devoted to special lectures, number about 18 annually. Fellows resident outside London may read before British Local Sections of the Society of Chemical Industry papers intended for subsequent publication in the Journal of the Chemical Society.

The annual subscription is £3. Those desiring to become Fellows of the Society should apply for further information to the Secretaries, Burlington House, London, W. 1.

CCXXI.—*The Properties of Ammonium Nitrate. Part IX. The Reciprocal Salt Pair Ammonium Nitrate and Lithium Chloride.*

By Edgar Philip Perman and Wilson Reginald Harrison.

In this investigation the same method was used as previously described, except that special means had to be devised to prevent the lithium salts from taking up moisture, owing to their great deliquescence. The salts were dried in a current of hot air at 150°, and transferred directly from the drying-oven to the experimental tube.

On increasing the proportion of lithium salt the stability was reduced, so that the range of the experiments at higher temperatures was very limited. On the other hand, very low melting points were obtained, the lowest being 84°. The range in this direction was therefore much increased, and on the whole it was possible to cover a wider field than in any of the other salt pairs investigated.

The following systems were studied, the last-mentioned constituent being the addendum :—

Binary Systems. (1) $NH_4NO_3 + LiNO_3$. (2) $NH_4NO_3 + NH_4Cl$.

Ternary Systems. (3) $(NH_4NO_3 + 5\%\ LiNO_3) + NH_4Cl$. (4) $(NH_4NO_3 + 10\%\ LiNO_3) + NH_4Cl$. (5) $(NH_4NO_3 + 15\%\ LiNO_3) + NH_4Cl$. (6) $(NH_4NO_3 + 20\%\ LiNO_3) + NH_4Cl$. (7) $(NH_4NO_3 + 25\%\ LiNO_3) + NH_4Cl$. (8) $(NH_4NO_3 + 30\%\ LiNO_3) + NH_4Cl$. (9) $(NH_4NO_3 + 32{\cdot}5\%\ LiNO_3) + NH_4Cl$. (10) $(NH_4NO_3 + 35\%\ LiNO_3) + NH_4Cl$. (11) $(NH_4NO_3 + 40\%\ LiNO_3) + NH_4Cl$. (12) $(NH_4NO_3 + 2{\cdot}5\%\ NH_4Cl) + LiNO_3$. (13) $(NH_4NO_3 + 4{\cdot}8\%\ NH_4Cl + LiNO_3$. (14) $(NH_4NO_3 + 7{\cdot}4\%\ NH_4Cl) + LiNO_3$.

It was not possible to examine the system lithium nitrate–lithium chloride, as it was found that molten lithium nitrate attacked the glass of the thermometer and of the containing tube, causing first an opalescence, and after some minutes' heating effecting the rapid disintegration of the glass. A platinum thermometer or thermo-couple would present the same difficulty, as some protective envelope would be necessary.

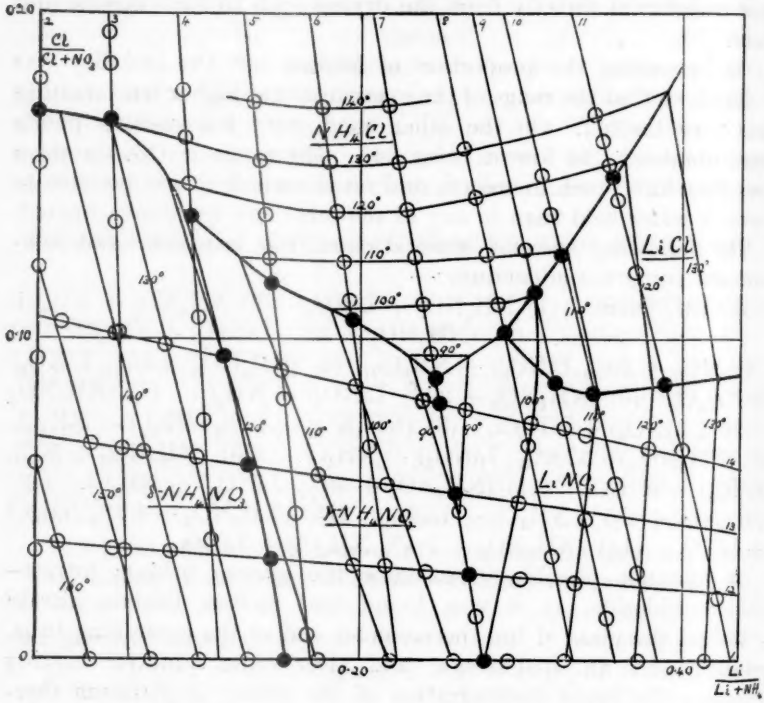
Curve 1 shows the usual two branches, with a eutectic at 97° at 25% lithium nitrate. There is, however, a marked break in the left branch at 122°, indicating a change (on cooling) from the δ to the γ form of ammonium nitrate. This is similar to that obtained by Lowry and Early with ammonium nitrate and sodium nitrate (J., 1922, **121**, 963).

A cooling curve was obtained for lithium nitrate (in a separate experiment) between 265° (its melting point) and 80°. It showed

no breaks, thus proving that this salt exists in but one crystalline form between these limits of temperature.

Curves 3, 4, 5, 6, and 7 are of the usual two-branch type, the solid phases being: left ammonium nitrate, right ammonium chloride.

The experiments recorded in curve 7, and in all curves passing near the ternary eutectic, show a great tendency to supercooling. On cooling the mixture below the initial freezing point, the temperature fell steadily to about 82° (sometimes lower) and then rose sharply to 84° or 85°, the ternary eutectic.



Curve 8 is of the same type, but the solid phases are lithium nitrate and ammonium chloride.

Curves 9, 10, and 11 show three branches, the solid phases being: left lithium nitrate, middle lithium chloride, right ammonium chloride.

Curves 12, 13, and 14 show a slight kink at the change of solid phase from δ- to γ-ammonium nitrate, and a break at the change to lithium nitrate. The whole of the results are summarised in the general diagram. It shows:

(1) Three ternary systems: (*a*) γ-Ammonium nitrate, lithium

nitrate, and ammonium chloride in equilibrium at 84°, T_1, the lowest melting point in this series of salt pairs.

This was confirmed by secondary arrests on curves 6, 7, 8, 9, 10, 12, 13, and 14. (*b*) Lithium nitrate, lithium chloride, and ammonium chloride in equilibrium at 95°, T_2. (*c*) δ-Ammonium nitrate, γ-ammonium nitrate, and ammonium chloride in equilibrium at 119°, T_3.

(2) Seven binary systems, *viz.* (*a*) δ-Ammonium nitrate and ammonium chloride, (*b*) γ-ammonium nitrate and ammonium chloride, (*c*) δ-ammonium nitrate and γ-ammonium nitrate, (*d*) γ-ammonium nitrate and lithium nitrate, (*e*) lithium nitrate and ammonium chloride, (*f*) lithium nitrate and lithium chloride, (*g*) lithium chloride and ammonium chloride.

The most noteworthy features are the lowness of the melting points obtained, the lowest being 84°, and the similarity of the system to that of the salt-pair ammonium nitrate and sodium chloride. There is no indication of the formation of any double salts or mixed crystals.

The complete system, if it could be realised, would be similar to the ammonium nitrate–sodium chloride system (Part VIII, J., 1922, **121**, 2476).

Summary.

(1) The freezing point of ammonium nitrate is lowered from 169° to 97° by lithium nitrate.

(2) An equilibrium diagram is given showing a ternary eutectic at 84° for γ-ammonium nitrate, lithium nitrate, and ammonium chloride, and two subsidiary ternary eutectics, *viz.*, lithium nitrate, lithium chloride, and ammonium chloride at 95°, and γ-ammonium nitrate, δ-ammonium nitrate, and ammonium chloride at 119°.

(3) No isomorphous mixtures or double salts are formed.

We are indebted to the Royal Society for a grant covering the greater part of the cost of this investigation, after Part IV.

Appendix.

Curve.						
(1)	% $LiNO_3$...	0·0	5·0	10·0	13·1	15·0	17·3
	F. pt.	169·5°	153·9°	135·6°	126·0°	121·1°	115·5°
	% $LiNO_3$...	20·0	25·0	30·0	35·0	40·0	45·0
	F. pt.	108·1°	97·0°	110·0°	124·0°	137·0°	155·5°
(3)	% NH_4Cl...	0·0	1·4	2·8	4·2	5·5	6·7
	F. pt.	154·0°	151·5°	148·7°	145·9°	142·9°	140·3°
	% NH_4Cl...	8·0	8·3	9·8	11·3	12·0	13·7
	F. pt.	138·1°	137·3°	134·0°	132·0°	130·5°	137·0°
	% NH_4Cl...	14·7	15·7				
	F. pt.	145·0°	154·0°				

Curve.							
(4)	% NH_4Cl...	0·0	1·5	3·0	4·3	5·6	6·9
	F. pt.	134·3°	131·8°	129·4°	126·6°	123·9°	121·2°
	% NH_4Cl...	8·3	9·5	10·7	11·8	12·9	13·9
	F. pt.	118·8°	116·2°	121·8°	130·7°	141·0°	149·0°
	% NH_4Cl...	14·9					
	F. pt.	157·0°					
(5)	% NH_4Cl...	0·0	1·2	2·3	3·5	4·6	5·7
	F. pt.	121·0°	118·3°	116·0°	114·3°	112·1°	110·0°
	% NH_4Cl...	6·8	7·8	8·8	9·8	11·1	12·4
	F. pt.	108·0°	106·0°	109·0°	119·0°	129·8°	138·0°
(6)	% NH_4Cl...	0·0	1·9	3·7	5·5	7·3	7·7
	F. pt.	108·0°	105·1°	102·5°	99·8°	96·5°	98·0°
	% NH_4Cl ...	8·4	10·1	11·8			
	F. pt.	103·8°	118·8°	136·0°			
(7)	% NH_4Cl...	0·0	1·4	2·5	2·8	4·1	5·4
	F. pt.	97·0°	96·1°	91·9°	91·0°	88·0°	86·2°
	% NH_4Cl...	6·9	8·1	10·0	11·6	13·2	14·7
	F. pt.	89·5°	101·2°	118·0°	132·0°	141·1°	155·5°
(8)	% NH_4Cl...	0·0	1·1	1·8	4·3	6·1	7·8
	F. pt.	110·0°	107·8°	105·6°	101·0°	97·7°	98·3°
	% NH_4Cl...	9·5	11·9	13·2	14·5		
	F pt.	112·0°	129·0°	140·0°	150·0°		
(9)	% NH_4Cl...	0·0	3·1	4·8	5·9	6·4	7·3
	F. pt.	116·0°	108·7°	106·2°	103·7°	104·0°	102·5°
	% NH_4Cl...	8·1	9·2	11·6	12·6		
	F. pt.	101·8°	109·3°	123·0°	129·3°		
(10)	% NH_4Cl...	0·0	2·3	3·5	4·7	5·1	5·9
	F. pt.	124·7°	119·5°	117·3°	113·5°	112·3°	110·0°
	% NH_4Cl...	6·3	6·7	7·8	8·0	8·6	9·3
	F. pt.	110·0°	110·0°	109·0°	109·0°	109·0°	109·0°
	% NH_4Cl...	10·1	10·4	13·0			
	F. pt.	113·3°	115·0°	134·0°			
(11)	% NH_4Cl...	0·0	3·2	5·6	7·4	8·5	9·6
	F. pt.	137·0°	132·3°	128·7°	126·7°	125·5°	123·7°
	% NH_4Cl...	10·6	11·7	12·6	13·7	14·7	
	F. pt.	120·7°	122·3°	129·0°	135·0°	142·0°	
(12)	% $LiNO_3$...	0·0	5·1	8·3	12·1	14·1	17·7
	F. pt.	163·5°	147·0°	135·4°	123·3°	118·1°	111·3°
	% $LiNO_3$...	19·1	20·1	22·6	24·7	26·4	28·8
	F. pt.	107·0°	104·5°	98·8°	92·6°	98·0°	105·0°
	% $LiNO_3$...	30·8					
	F. pt.	112·5°					
(13)	% $LiNO_3$...	0·0	4·3	6·7	9·2	12·4	14·6
	F. pt.	158·9°	145·7°	137·0°	128·0°	117·0°	112·5°
	% $LiNO_3$...	17·1	19·3	20·7	23·0	25·0	26·9
	F. pt.	106·8°	101·3°	98·0°	92·9°	94·0°	97·8°
	% $LiNO_3$...	28·4	29·0	31·1	33·9	36·5	39·6
	F. pt.	101·8°	102·8°	106·8°	114·6°	125·7°	140·0°

Curve.						
(14) % $LiNO_3$...	0·0	1·7	4·6	7·2	9·9	12·8
F. pt.	153·5°	147·0°	138·5°	129·3°	120·7°	113·6°
% $LiNO_3$...	15·4	19·4	21·7	22·9	23·9	25·4
F. pt.	108·0°	98·0°	92·6°	89·3°	88·2°	92·8°
% $LiNO_3$...	27·9	29·4	32·6			
F. pt.	97·0°	102·3°	109·3°			

UNIVERSITY COLLEGE, CARDIFF. [*Received, June 18th*, 1924.]

CCXXII.—*Electrolytic Formation of Alloys and Amalgams of Manganese.*

By ALAN NEWTON CAMPBELL.

As manganese has recently been deposited electrolytically in a state of purity (Allmand and Campbell, *Trans. Faraday Soc.*, Feb., 1924), it was thought to be of interest to determine whether alloys of that metal could be produced electrolytically by the usual methods, *viz.*: (1) Discharge of $Mn^{\cdot\cdot}$-ion at a cathode consisting of the other metal (Haber and Sack, *Z. Elektrochem.*, 1902, **8**, 245); (2) simultaneous discharge of two ions (see Schoch and Hirsch, *J. Amer. Chem. Soc.*, 1904, **29**, 314, for a good example of the latter in the case of zinc and nickel).

The former method is chiefly of theoretical interest. It was shown by Haber and Sack (*loc. cit.*) that considerable lowering of the discharge potential (depolarisation) takes place at certain cathodes. In the case where the discharged ion forms a solid solution or a series of mixed crystals with the other metal, this lowering is approximately proportional to the amount of the more positive metal in the alloy. Very considerable depolarisation, however, takes place when a true compound is formed which dissolves in excess of the more positive metal.

The latter method is of more technical application. The composition of the deposited alloy is dependent to some extent on variations in the composition of the electrolyte, but this can be overcome by having large bulks of electrolyte. It was observed by Schoch and Hirsch that although zinc possesses a more negative equilibrium potential than nickel, the alloys they obtained (at 25°) contained always more zinc than nickel. Attention has more recently been drawn to this point by Foerster ("Elektrochemie wässeriger Lösungen," 1922 ed.), who finds that whilst it holds invariably at low temperatures, at high temperatures and with reduced current density the deposited alloy contains more nickel than zinc. When, however, at the same high temperature the current density is increased, the alloy again contains zinc in excess.

This is readily explicable on the ground of the well-known reaction resistance to nickel deposition. This is too high at room temperature to admit of pure nickel deposition, and an alloy rich in zinc is deposited at a potential less negative than that of zinc. At higher temperatures, the reaction resistance is reduced, and at low current densities, nickel or an alloy rich in nickel is deposited. At higher current densities, the reaction resistance again sets in, the potential of the cathode suddenly becomes more negative, and the zinc-rich alloy is deposited. It was thought it would be of interest to investigate if such a phenomenon occurs in the case of manganese and nickel or iron.

Experimental.

1. *Amalgams.*

The apparatus used consisted of a rectangular glass trough, 25 × 15 × 15 cm., containing 4 litres of electrolyte. The anodes were of platinum sheet suspended in porous pots. The cathode was a dish of mercury, placed on the floor of the trough. The area of the mercury surface was 21·24 sq. cm. A vertical glass stirrer was used, stirring the mercury of the cathode as well as the electrolyte, to ensure uniform composition of the cathode during potential measurements. Two anodes were used, symmetrically placed with respect to the cathode, to ensure, as far as possible, uniform distribution of current. Each anode was connected to a separate ammeter, and each carried equal current. The composition of the electrolyte was: 300 gms. of $MnSO_4,4H_2O$ per litre: 100 gms. of $(NH_4)_2SO_4$ per litre ("standard" electrolyte). The liquid in the anode pots was saturated ammonium sulphate solution.

The potential of the cathode was determined by means of a normal calomel electrode, connected to a Lugin capillary. The tip of the capillary was just above the surface of the mercury, in each experiment. The *E.M.F.* of the combination was determined by Poggendorff's method, using a delicate mirror galvanometer in place of the usual capillary electrometer.

The temperature was that of the room (11·5°). The current was taken from the main through a lamp resistance and sliding rheostat. In the first experiment the current was steadily increased, over a period of about 3 hours, and the potential of the cathode measured for each increase. The current density was raised from 0·282 amp./dcm.^{2} to 0·800 amp./dcm.^{2}, and the cathode potential, commencing at −1·092 volts (abs.), fell in an irregular manner to −1·362 volts (abs.) at 0·800 amp./dcm.^{2}. At current density 0·377 amp./dcm.^{2}, and potential −1·202 volts, incipient evolution of hydrogen commenced.

It was impossible to get constant readings unless the mercury was stirred. After the last reading, recorded above, the experiment was continued for 6 hours, when the mercury had attained a semi-solid or pasty condition. This amalgam had no apparent action on the electrolyte; even when it was treated with concentrated hydrochloric acid, hydrogen was evolved only very slowly, probably owing to the high hydrogen overvoltage at a mercury surface. After standing under concentrated hydrochloric acid for 24 hours, it was still semi-solid.

The absence of sudden changes in cathode potential seemed to indicate formation of only one compound, or solution, etc., at the current densities used. The next experiment was conducted at constant current density.

Experiment 2.—Temp. 9°. Current density, 0·5 amp./dcm.^{2}. Current efficiency, 47·4%.

The amalgam obtained was, as before, semi-solid. It was not uniform, for distinct lumps could be felt in it. It could only be decomposed by prolonged boiling with concentrated hydrochloric acid. During the run, the potential of the cathode was determined at intervals of one hour. The current was then stopped for a few minutes and the equilibrium potential taken. The difference between the two values may be designated "reaction resistance," for want of a better term, although it is probably in many cases largely ordinary electrical resistance, due to a film of gas. The following are the potentials (volts abs.) observed:

Current on ...	−0·885	−0·909	−1·135	−1·028	−0·995	Mean −0·9904
Current off ...	−0·631	−0·631	−0·631	−0·631	−0·631	

Mean "reaction resistance" = 0·3594 volt.

The potential values during current flow oscillated considerably, probably owing to variations in conductivity of the gas film. The first rapid fall of potential on switching off the current was followed by a very slow fall (compare Allmand and Campbell, *loc. cit.*), approaching a minimum equilibrium value at −0·631 volt. The potential of pure manganese in presence of manganese ions of the concentration of the electrolyte is −0·793 volt (abs.). Hence depolarisation at the mercury surface is marked but not great. Moreover, since the equilibrium potential was constant, it seemed necessary to assume that the mercury soon becomes saturated with manganese. Excess of manganese, or of manganese–mercury compound, then separates out, imparting to the mass its pasty consistency. To test this hypothesis, three experiments of different duration were carried out. In each, the final minimum equilibrium potential was determined, the mercury then filtered through a perforated filter-paper, to remove solid matter, and the liquid

phase analysed for manganese. The manganese was separated from the mercury by dissolution in boiling concentrated hydrochloric acid, in contact with platinum foil, and estimated in the usual way with bromine and ammonia. In this way also the current efficiency of experiment 2 was calculated.

Exp. No.	Duration (hours).	Equilibrium potential.	% Mn in liquid phase.
3	1	−0·631 volt (abs.)	0·0046
4	2	−0·631 „	0·0034
5	3	−0·631 „	0·0038

The amount of manganese in the liquid phase does not of course represent the total amount of manganese deposited; the amount of solid matter left in the filter being greater, the longer the duration of the experiment. It is shown, however, that constancy of equilibrium potential is correlated with constancy of composition of the liquid phase.

2. *Discharge on a Depolarising Cathode.*

Lead, in the form of assay lead foil, was used for this experiment, other workers having found that this metal can even depolarise the discharge of the alkali metals. The other experimental details were as before.

Experiment 6.—Temp. 8°. Current density, 15 amp./dcm.^{2}.

The deposit obtained was hard, dead black, and had "sprouted" round the edges. It was found to be 100 per cent. manganese, containing the merest trace of lead. The metallic content of the deposit was estimated by solution in hydrochloric acid, and, after evaporation with sulphuric acid, precipitation with bromine and ammonia in the usual way. The equilibrium potential was that of pure manganese, −0·793 volt. Here there is evidently no alloy formation of any kind.

Further experiments with depolarising cathodes were not undertaken, as they would not have been of value for the production in bulk either of alloys of manganese or of pure manganese. Experiments were now undertaken with mixed electrolytes.

Deposition from Mixed Electrolytes.

Manganese–Nickel Electrolyte.—The electrolyte consisted of 2 litres of "standard" manganese sulphate electrolyte mixed with 2 litres of nickel ammonium sulphate solution, containing 93 gms. $NiSO_4,(NH_4)_2SO_4,6H_2O$ per litre. The electrolyte was neutral.

A rectangular copper cathode, bordered with "Formite" insulating varnish, was used. Copper had previously been found

not to alloy with manganese during deposition (Allmand and Campbell, *loc. cit.*).

A series of experiments was carried out at increasing current densities, with the intention of detecting the "Foerster" effect, alluded to in the introduction, if such existed. These experiments are summarised in the following table.

Exp.	Temp.	Current dens. (amp./dcm.²).	% Total curr. eff.	Appearance of deposit.	% Mn in deposit.
7	11°	1·0	65·0	Loose, "warty," bright.	0·0
8	14	2·0	47·8	Uneven, rough, adherent.	8·86
9	9	4·0	16·7	Dull, compact.	6·82
10	11·5	8·0	14·35	Bright, smooth.	9·39
11	14	16·0	10·42	Bright, pitted.	12·27

The following are the mean potentials (volt abs.) during the experiments:

Expt.	7	8	9	10	11
Current on	−0·503	−0·594	−0·523	−0·5775	−0·9805
Current off	−0·0434	−0·0584	−0·074	−0·1987	−0·2905

A certain amount of manganese depolarisation obviously does take place, but there is no indication of a "Foerster" effect (see introduction). The calculated equilibrium potential $Ni/Ni^{\cdot\cdot}$ in this electrolyte is +0·033 volt (abs.), whilst that actually found in the seventh experiment, where the deposit was pure nickel, was −0·0434 volt (abs.) and apparently constant, after an initial rapid fall. This has been observed in so many cases that it is thought to be a kind of passivity; it has, moreover, been observed by other investigators. It was also observed that the deposition potential was much higher at the commencement than at the finish of an experiment. The equilibrium potential is not directly proportional to the manganese content of the deposit. The decrease in current efficiency with increase in current density is remarkable and is probably due to the fact that the hydrogen overvoltage does not increase as rapidly as the reaction resistance to nickel deposition.

Manganese–Iron Electrolyte.—A similar experiment to the last of the preceding series was carried out, using an electrolyte containing 2 litres of "standard" manganese sulphate electrolyte, and 2 litres of ferrous ammonium sulphate solution containing 56 gms. of iron per litre. The surface of the electrolyte was covered with a layer of paraffin oil, to prevent oxidation.

Experiment 12.—The data are: temp. 14°; acidity 0·09*N*; current density 16·0 amps./dcm.²; total current effic. 21·18%; appearance of deposit, hard and adherent; percentage of iron in the deposit 91·85.

The appearance of the deposit was remarkable. It had a lustre like bismuth and presented the appearance of fused metal. It was hard enough to scratch glass, and adherent, and did not "flake" during deposition, despite a vigorous hydrogen discharge, nor did the deposit rust on keeping, as electrolytic iron does. It could not be polished with emery, probably on account of its hardness.

On the other hand, deposition from the same electrolyte on a rotating brass cathode, using a burnisher of vulcanite, yielded a smooth deposit consisting of non-adherent strata. Deposition was accompanied by "flaking" in this case. This deposit, on being placed in a partial vacuum, disrupted owing to the escape of hydrogen. It also rusted rapidly.

The mean potentials (volt abs.) of the cathode were: current on, −0·574; current off, −0·250.

There is apparently no "Foerster" effect, the deposit containing a large excess of the more positive constituent.

Manganese and Zinc Electrolyte.—In these experiments a rotating aluminium cathode was used, the Lugin capillary being distant about 1 mm. from the surface. The electrolyte consisted of 2 litres of "standard" manganese sulphate solution, mixed with 2 litres of zinc sulphate solution, containing 180 gms. of $ZnSO_4,7H_2O$ and 100 gms. of $(NH_4)_2SO_4$ per litre. The electrolyte was neutral.

Expt. No.	Temp.	Current dens. (amps./dcm.²).	% Total curr. eff.	Appearance of deposit.	Mn in deposit.
13	10·5°	4·0	100	Smooth, bright.	Nil.
14	7	8·0	86·94	"Warty," blistered.	Nil.
15	12	16·0	80·4	"Treeing" and "flaking."	Trace.

The following are the mean potentials (volt abs.) of the cathode:

Expt.	13	14	15
Current on	−0·813	−0·853	−0·896
Current off	−0·519	−0·519	−0·519

There is apparently here no depolarisation of manganese deposition. It is interesting to note that adherent and apparently pure deposits of zinc can be obtained, at 100% current efficiency, from comparatively dilute solutions of zinc, by means of a rotating cathode. The addition of the ammonium sulphate would of course tend to keep the deposit pure.

Manganese and Aluminium Electrolyte.—This experiment was really an attempt to depolarise aluminium discharge by means of manganese. A rotating aluminium cathode was used. The electrolyte consisted of 2 litres of standard manganese sulphate electrolyte mixed with 2 litres of aluminium sulphate solution, containing 150 gms. of $Al_2(SO_4)_3$ anhyd. per litre and 100 gms. $(NH_4)_2SO_4$

per litre. The temperature was 11° and the current density 15 amp./dcm.^{2}.

The experiment failed entirely. A hydrated mass was obtained, apparently consisting of mixed aluminium and manganese hydroxides, so badly conducting that at the end of the experiment the current had fallen to 0·4 amp. The mass smelled very strongly of ammonia, probably owing to violent hydrogen discharge at the cathode, followed by absorption of the ammonia by the colloidal mass. Aluminium hydroxide is precipitated at about the neutrality point, p_H 7, and hence the buffer action of the ammonium sulphate cannot come into play.

Summary.

1. The electrolytic production of manganese amalgam has been studied electromotively.

2. It has been shown that manganese is deposited on a lead cathode without depolarisation.

3. Alloys of manganese and nickel, and of manganese and iron, can be obtained by deposition from mixed electrolytes. These alloys are of low manganese content. There is no indication of a "Foerster" effect.

4. An unsuccessful attempt to depolarise aluminium discharge by means of manganese has been made.

In conclusion, the author wishes to acknowledge his indebtedness to Prof. A. J. Allmand for a constructive criticism of this work.

KING'S COLLEGE,
UNIVERSITY OF LONDON. [*Received, April 7th*, 1924.]

CCXXIII.—*Electrometric Studies on Azo- and Hydrazo-compounds.*

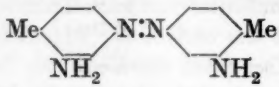
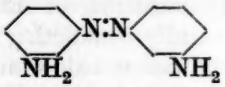
By EINAR BIILMANN AND JAKOB H. BLOM.

ALTHOUGH the affinity of a chemical process may be measured by the electromotive force set up by the change, very few such measurements have yet been carried out for organic compounds. The object of this paper is to record the results of electrometric experiments on the reduction process

$$R{\cdot}N{:}NR + H_2 \rightleftharpoons R{\cdot}NH{\cdot}NHR.$$

The methods employed were substantially those of Biilmann (*Ann. Chim.*, 1921, [ix], **15**, 109), and of Biilmann and Lund (*ibid.*, **16**, 321; **19**, 137). As neutral azo- and hydrazo-compounds are only very sparingly soluble in aqueous solvents, it was decided to

employ their amino-derivatives, and accordingly the compounds 3 : 3′-diamino-4 : 4′-dimethylazobenzene (I), and 3 : 3′-diaminoazobenzene (II), and their corresponding hydrazo-compounds were

(I.)  (II.) 

used. These are referred to in the paper as azotoluidine, azoaniline, hydrazotoluidine, and hydrazoaniline, respectively.

Because of the ease of oxidation of the hydrazo-compounds, it was found necessary to conduct the experiments in an oxygen-free atmosphere, and, further, because of the fact that the hydrazo-compounds in acid solution undergo a semidine or benzidine change, thus removing hydrazo-compound from the cell, a steady change of potential with time was always observed. This fact necessitated the examination of the time–*E.M.F.* function of the cells in order that the value of the *E.M.F.* at zero time might be obtained by extrapolation. This was not entirely disadvantageous, as it rendered possible a determination of the velocity coefficients of the inversion of the hydrazo-compounds. The change of *E.M.F.* with time was found to be linear.

The Measurement of the Reduction Potentials.

The method employed involved the measurement of the *E.M.F.* of the chains

$$+\ \mathrm{Pt}\ \Big|\ \text{Quinhydrone, electrolyte, } \frac{\text{azo-compound}}{\text{hydrazo-compound}}\ \Big|\ \mathrm{Pt}\ -$$

at different times. These voltages are denoted in the tables by the symbol ϕ, and graphical extrapolation from these figures gave values for ϕ_0, the potential at zero time. The standard electrode consisted of a quinhydrone element as described by Biilmann (*Trans. Faraday Soc.*, 1923, **19**, 676) containing the same electrolyte as the azo–hydrazo electrode in order to avoid liquid junction potentials. The potentials, ψ, of these standard electrodes were determined, and are collected in Table I. As ψ is the *E.M.F.* of a cell of the type

$$+\ \mathrm{Pt}\ \Big|\ \text{Quinhydrone, electrolyte, hydrogen}\ \Big|\ \mathrm{Pt}\ -$$

it follows that the required reduction potential, π_0, which is the *E.M.F.* of the combination

$$+\ \mathrm{Pt}\ \Big|\ \frac{\text{Azo-compound}}{\text{Hydrazo-compound}}\text{, electrolyte, hydrogen}\ \Big|\ \mathrm{Pt}\ -$$

will be given by the equation

$$\pi_0 = \psi - \phi_0.$$

TABLE I.

The Quinhydrone–Hydrogen Electrode.

Temp.	Electrolyte.	*E.M.F.* (ψ) in volt.
18·0°	0·1*N*-HCl	0·7044
18·0	0·2*N*-HCl	0·7039
18·0	(0·1*N*-HCl, 0·1*N*-KCl)	0·7039
25·0	0·1*N*-HCl	0·6990
37·0	0·1*N*-HCl	0·6900
37·0	(0·1*N*-HCl, 0·5*N*-KCl)	0·6891
37·0	0·6*N*-HCl	0·6887

The potentials of the electrode under the last two conditions are not quite steady, but decrease by about 0·3 millivolt per hour. The experimental results, however, have been corrected for this effect.

The original solutions were made equimolar (generally 0·002—0·004 molar) in azo- and hydrazo-compound; the electrolytes employed as solvents and the temperatures are recorded in Table I. The results are given in Tables II—XI.

TABLE II.

Azotoluidine = Hydrazotoluidine = 0·00208 mol.
Temp. = 18°. Solvent 0·1*N*-HCl.

Two blank platinum electrodes.

t (mins.).	ϕ I.	$k \times 10^3$.	t (mins.).	ϕ II.	$k \times 10^3$.
8·0	0·3237		10·2	0·3218	
12·3	0·3199		19·3	0·3132	76
16·3	0·3161	76	27·5	0·3056	75
21·5	0·3110	77	31·8	0·3015	75
25·4	0·3072	77	33·5	0·2998	75
29·4	0·3034	77	37·6	0·2960	75
36·8	0·2962	77	42·7	0·2911	75
39·8	0·2931	78	44·5	0·2895	75
			47·0	0·2870	75
			50·0	0·2840	76

$\phi_0 = 0·3314$; $k \times 10^3 = 76$.

TABLE III.

Azotoluidine = Hydrazotoluidine = 0·00208 mol.
Temp. = 18°. Solvent 0·1*N*-HCl.

Two blank platinum electrodes.

t (mins.).	ϕ I.	$k \times 10^3$.	t (mins.).	ϕ II.	$k \times 10^3$.
16·4	0·3155		13·7	0·3181	
20·4	0·3117	76	18·6	0·3137	72
24·7	0·3077	75	21·7	0·3107	74
30·7	0·3020	75	28·3	0·3044	75
34·7	0·2983	75	32·7	0·3004	74
38·9	0·2942	76	36·7	0·2965	75
40·7	0·2927	75	45·0	0·2886	75
50·0	0·2840	75	46·9	0·2868	75
54·3	0·2801	75	52·1	0·2820	75
60·5	0·2752	73	58·3	0·2770	73
			63·4	0·2728	73

$\phi_0 = 0·3309$; $k \times 10^3 = 75$.

TABLE IV.

Azotoluidine = Hydrazotoluidine = 0·00209 mol.
Temp. = 18°. Solvent 0·1*N*-HCl, 0·1*N*-KCl.

Two blank platinum electrodes.

t (mins.).	ϕ I.	$k \times 10^3$.	t (mins.).	ϕ II.	$k \times 10^3$.
12·3	0·3208		14·1	0·3190	
16·4	0·3168	73	18·7	0·3150	72
22·3	0·3118	72	24·3	0·3100	72
26·2	0·3082	72	28·0	0·3067	72
31·0	0·3038	73	32·1	0·3028	73
35·1	0·3000	73	36·4	0·2987	73
39·2	0·2961	73	41·6	0·2938	74
46·2	0·2892	74	48·0	0·2874	75
51·8	0·2838	75	59·5	0·2764	75
54·5	0·2811	75			
64·5	0·2710	76			

$\phi_0 = 0{\cdot}3320$; $k \times 10^3 = 73$.

TABLE V.

Azotoluidine = Hydrazotoluidine = 0·00208 mol.
Temp. = 18°. Solvent 0·2*N*-HCl.

Two blank platinum electrodes.

t (mins.).	ϕ I.	$k \times 10^3$.	t (mins.).	ϕ II.	$k \times 10^3$.
8·1	0·3200		5·8	0·3233	
11·8	0·3148	107	9·7	0·3178	110
16·3	0·3087	110	14·0	0·3118	111
20·0	0·3037	109	18·1	0·3262	110
24·3	0·2976	110	22·1	0·3008	109
28·7	0·2915	111	27·2	0·2937	110
31·8	0·2871	111	30·2	0·2895	110
34·9	0·2829	110	33·3	0·2850	111
40·4	0·2751	111	36·9	0·2800	111
			42·0	0·2732	110

$\phi_0 = 0{\cdot}3312$; $k \times 10^3 = 110$.

TABLE VI.

Azotoluidine = Hydrazotoluidine = 0·00208 mol.
Temp. = 18°. Solvent 0·2*N*-HCl.

Two blank platinum electrodes.

(mins.).	ϕ I.	$k \times 10^3$.	t (mins.).	ϕ II.	$k \times 10^3$.
8·0	0·3200		10·3	0·3166	
11·6	0·3150	111	15·2	0·3100	111
19·8	0·3035	112	17·2	0·3075	109
24·0	0·2975	113	21·2	0·3015	112
28·4	0·2915	112	25·8	0·2950	112
31·9	0·2865	112	30·1	0·2890	112
36·1	0·2801	112	33·9	0·2836	113
44·5	0·2694	110	40·1	0·2750	112
51·4	0·2604	113	47·8	0·2643	112
			58·8	0·2485	113

$\phi_0 = 0{\cdot}3312$; $k \times 10^3 = 112$.

TABLE VII.

Azotoluidine = Hydrazotoluidine = 0·00295 mol.
Temp. = 25°. Solvent 0·1*N*-HCl.

One blank platinum electrode.

t (mins.).	ϕ.	$k \times 10^3$.	t (mins.).	ϕ.	$k \times 10^3$.
11·8	0·299		21·2	0·270	241
12·8	0·296	234	22·9	0·265	238
16·2	0·285	248	24·8	0·260	234
18·0	0·279	252	28·6	0·250	227
19·5	0·275	243			

$\phi_0 = 0·335$; $k \times 10^3 = 240$.

TABLE VIII.

Azoaniline = Hydrazoaniline = 0·00235 mol.
Temp. = 18°. Solvent 0·1*N*-HCl.

Gilt platinum with platinum black.

	ϕ.		$k \times 10^5$.	
t (mins.).	I.	II.	I.	II.
1605	0·2875	0·2872		
2880	0·2829	0·2827	27·5	28·2
3110	0·2819		28·8	
3240		0·2814		28·3
4300	0·2778	0·2776	28·7	28·4
4830	0·2761	0·2761	28·2	27·2
5770	0·2709	0·2710		

$\phi = 0·2931$; $k \times 10^5 = 28·2$.

TABLE IX.

Azoaniline = Hydrazoaniline = 0·00235 mol. ϕ I.
0·00236 ,, ϕ II.
Temp. = 37°. Solvent 0·1*N*-HCl.

Two blank platinum electrodes.

t (mins.).	ϕ I.	$k \times 10^5$.	t (mins.).	ϕ II.	$k \times 10^5$.
214	0·2851		47	0·2863	
246	0·2840	210	74	0·2854	225
294	0·2826	213	100	0·2846	233
343	0·2817	192	131	0·2835	225
384	0·2805	197	141	0·2831	220
413	0·2796	201	188	0·2814	215
440	0·2793	190	216	0·2807	222
476	0·2783	192	218	0·2803	213
490	0·2779	193	267	0·2786	214
526	0·2769	194	300	0·2775	215
602	0·2735	219	332	0·2773	237
618	0·2728	223	342	0·2761	217
644	0·2721	222	367	0·2758	228
712	0·2703	219	372	0·2747	210
720	0·2701	218	410	0·2736	214
724	0·2702	215			

$\phi = 0·2905$; $k \times 10^5 = 207$. $\phi_0 = 0·2882$; $k \times 10^5 = 221$.

TABLE X.

Azoaniline = Hydrazoaniline = 0·00237 mol.
Temp. = 37°. Solvent 0·1*N*-HCl, 0·5*N*-KCl.
Gilt platinum electrodes with platinum black.

	ϕ.		$k \times 10^5$.	
t (mins.).	I.	II.	I.	II.
33	0·2886	0·2881		
56	0·2877	0·2875	293	
86	0·2865	0·2864	296	
116	0·2854	0·2852	289	299
136	0·2847		293	
137		0·2844		294
170	0·2833	0·2833	290	284
202	0·2820	0·2818	292	297
230		0·2808		291
234	0·2807		294	
263	0·2796		293	
265		0·2796		284
291	0·2786	0·2786	290	284
327	0·2772	0·2771	290	288
350	0·2764	0·2764	288	283
429	0·2733	0·2732	289	287
465	0·2719	0·2720	289	284
500	0·2705	0·2705	296	287
530	0·2692	0·2693	294	288
		ϕ_0 = 0·2899.	Average = 290.	

TABLE XI.

Azoaniline = Hydrazoaniline = 0·00236 mol.
Temp. = 37°. Solvent 0·6*N*-HCl.
Gilt platinum electrodes with platinum black.

	ϕ.		$k \times 10^5$.	
t (mins.).	I.	II.	I.	II.
45	0·2843	0·2841		
77	0·2817		608	
78		0·2814		612
91	0·2806	0·2804	602	602
106	0·2793	0·2791	613	613
122	0·2780	0·2778	612	612
135	0·2769	0·2766	615	622
151	0·2756	0·2754	613	613
167	0·2742		619	
168		0·2739		625
181	0·2731	0·2729	616	616
196	0·2720	0·2717	609	613
243	0·2680	0·2679	616	616
270	0·2656	0·2654	622	622
301		0·2629		620
302	0·2630		620	
		ϕ_0 = 0·2880.	Average = 615.	

As the reduction potentials of the azo–hydrazo electrodes were to be measured with respect to hydrogen electrodes of the same acidity, it was necessary to correct the observed values for the decreased acidity of the solution caused by salt formation between

the acid of the electrolyte and the amino-groups of the solutes. This correction is obviously given by the equation

$$\Delta\pi = 0{\cdot}0001983T \log_{10} C_1/C_2,$$

where C_1 is the hydrogen-ion concentration of the solvent, and C_2 that of the solution, and the correction is to be added to the observed results. As the azo- and hydrazo-compounds contain two amino-groups each, and the acid is present in large excess, the decrease in normality of the acid solvent by combination with the basic groups of the solutes may be obtained by multiplying the molar concentration of either of the solutes (present originally in equal quantity) by 4. The hydrogen-ion concentrations (or activities) of solvent and solution are not identical, of course, with their molar concentrations of acid, but as the concentrations are so nearly equal, the *ratio* of one will be, within the limit of experimental error, the ratio of the other, so that it is permissible to write molar instead of ionic concentrations in the above equation.

The whole of the experimental results are summarised in Tables XII and XIII, and it is submitted that the determinations are sufficiently exact to permit of the deduction that the difference, for example, between the π_0 (corr.) values for azo–hydrazotoluidine in 0·1*N*-HCl and in 0·2*N*-HCl or (0·1*N*-HCl, 0·1*N*-KCl) may be explained as an influence of the electrolytes on the activities of the azo- and hydrazo-compounds. A similar effect has been observed in the case of quinhydrone.

TABLE XII.

Azotoluidine–Hydrazotoluidine.

Temp.	Molar conc.	Solvent.	Corr. acidity.	$\Delta\pi$.	π_0.	π_0 corr.	$k \times 10^3$.	$t_{\frac{1}{4}}$. Half conc. Mins.
18°	0·00208	0·1*N*-HCl	0·092*N*	0·0021	0·3730	0·3751	76	9·1
,,	,,	,,	,,	,,	0·3735	0·3756	75	9·2
,,	0·00209	0·1*N*-HCl + 0·1*N*-KCl	,,	,,	0·3719	0·3740	73	9·9
,,	0·00208	0·2*N*-HCl	0·192*N*	0·0010	0·3727	0·3737	110	6·3
,,	,,	,,	,,	,,	0·3727	0·3737	112	6·2
25	0·00295	0·1*N*-HCl	0·088*N*	0·0033	0·3640	0·3673	240	2·9

TABLE XIII.

Azoaniline–Hydrazoaniline.

Temp.	Molar conc.	Solvent.	Corr. acidity.	$\Delta\pi$.	π_0.	π_0 corr.	$k \times 10^5$.	$t_{\frac{1}{4}}$. Half conc. Mins.
18°	0·00235	0·1*N*-HCl	0·091	0·0024	0·4113	0·4137	28·2	2458
37	,,	,,	,,	0·0025	0·3995	0·4020	207	335
,,	0·00236	,,	,,	,,	0·4018	0·4043	221	314
,,	0·00237	0·1*N*-HCl + 0·5*N*-KCl	,,	,,	0·3992	0·4017	290	239
,,	0·00236	0·6*N*-HCl	0·591	0·0004	0·4007	0·4011	615	113

By means of the equation

$$\pi_0 \text{ (corr.)} = 0{\cdot}0000992T \log (P_{H_2}/P)$$

we can calculate from the potentials thus determined the hydrogen pressure, P, which produces the same effect as a mixture of equimolar quantities of azo- and hydrazo-compound.

For $T = 291°$ Abs. and hydrogen pressure, P_{H_2}, $= 1$ atmosphere, we get

π_0 (corr.) $= 0{\cdot}3754$ for azo–hydrazotoluidine, and
$= 0{\cdot}4137$ for azo–hydrazoaniline, in each case with $0{\cdot}1N$-hydrochloric acid as solvent, whence,

for azo–hydrazotoluidine, $P = 10^{-13{\cdot}0}$ atmosphere, and
for azo–hydrazoaniline, $P = 10^{-14{\cdot}3}$ atmosphere.

For benzoquinone-quinhydrone and alloxantin, the corresponding hydrogen pressures at $T = 291°$ Abs. are found to be $10^{-21{\cdot}4}$ and $10^{-12{\cdot}8}$ atmosphere, respectively.

The Velocity Coefficients of the Rearrangement of Hydrazo-compounds.

In the earlier part of the paper it was pointed out that the potentials of the azo–hydrazo electrodes change with time. They decrease with respect to the quinhydrone electrode, to which they are negative, and consequently increase with respect to the hydrogen electrode, to which they are positive. This effect may be explained by the transformation of the hydrazo-compound to a semidine or a benzidine, that is to say, by the decrease of the "hydrogen pressure" due to the hydrazo-compound.

If we put A_t and $A_{t'}$, H_t and $H_{t'}$, and π_t and $\pi_{t'}$ as the concentrations of the azo- and hydrazo-compound, and the corresponding potentials relative to the hydrogen electrode, respectively, at times t and t', we have,

$$\pi_{t'} - \pi_t = \frac{RT}{nF} \log_e \frac{A_{t'} \cdot H_t}{A_t \cdot H_{t'}}$$

or, since the concentration of the azo-compound is unaltered ($A_t = A_{t'}$),

$$\pi_{t'} - \pi_t = \frac{RT}{nF} \log_e \frac{H_t}{H_{t'}} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If now we suppose that the rearrangement of the hydrazo-compound in the presence of a constant concentration of catalyst obeys the law for a unimolecular reaction, the velocity coefficient of the change is given by the equation

$$k = \frac{1}{t' - t} \log_e \frac{H_t}{H_{t'}} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Combining (1) and (2),

$$k = \frac{nF}{RT} \cdot \frac{\pi_{t'} - \pi_t}{t' - t} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In this equation, $n = 2$, $T = 291°$, $298°$, or $310°$, and R and F have their usual significance. The factor nF/RT assumes the following values: 79·76 at 291°, 77·89 at 298°, and 74·87 at 310° Abs. The value of k has been calculated by means of equation (3) from the experimental figures, and it will be seen from Tables XII and XIII that it increases with temperature and with hydrogen-ion concentration, but that it is by no means proportional to the latter. From Tables II and III, it will be seen that the constancy of k calculated from numerous observations at the same temperature and hydrogen-ion concentration is very satisfactory. It will be observed, moreover, that k for hydrazotoluidine is very much greater than for hydrazoaniline. To bring out this point, the times required for the concentration of the hydrazo-compound to fall from one value to one-half of this value are given in minutes in Tables XII and XIII under the heading $t_{\frac{1}{2}}$. In comparing the velocities of rearrangement of the hydrazo-compounds, it should be remembered that the two processes are not quite identical: hydrazotoluidine probably gives a semidine, whilst hydrazoaniline gives a benzidine. It appears, too, that the rearrangement with the higher velocity coefficient gives rise to more well-defined values of the potential than the other, and also, as would be expected, that rise of temperature produces the same effect, because of the influence of the temperature on the velocity.

Although it was considered exceedingly probable that the potential change was due to the inversion of the hydrazo-compound, this point was tested experimentally, with results which are collected in Table XIV. The concentrations of azo- and hydrazoaniline in this case were adjusted initially in the ratio of 1 to 10. It will be seen that the value of π_0 (corr.) in this case is 0·3857 volt, whilst the corresponding value for equimolar proportions is 0·4137 volt (Table XIII). The difference is 0·0280 volt, in satisfactory agreement with the theoretical value of 0·0289 volt, thus furnishing proof of this hypothesis. Further evidence on this point was obtained by chemical means. A solution of 0·1797 gm. of hydrazotoluidine in 108 c.c. of 0·1*N*-hydrochloric acid was kept at 18° for 10 minutes, and was then titrated with 0·1*N*-iodine solution. It was found to contain 0·1115 gm. of hydrazotoluidine. From this figure, the velocity coefficient is calculated to be 48×10^{-3}, a value of the same order as 76×10^{-3} given in Table XII. The agreement is satisfactory when it is remembered that the polyamine produced by the rearrangement takes up iodine under these conditions, thus giving too high a value for the residual hydrazo-compound, that is to say, too low a value for k. Further, it appears probable that the presence of azo-compound affects the velocity of the change.

TABLE XIV.

Azoaniline 0·000486 mol. Hydrazoaniline 0·00486 mol.
Temp. = 18°. Solvent 0·1*N*-HCl.

Gilt platinum electrodes with platinum black.

	ϕ.		$k \times 10^5$.	
t (mins.).	I.	II.	I.	II.
145	0·3213	0·3203		
1440	0·3184	0·3179	17·8	14·8
1605	0·3180	0·3174	18·0	15·8
2715	0·3146	0·3139	20·8	19·9
2880	0·3143	0·3136	20·4	19·5
3080	0·3141	0·3133	19·5	19·0
4170	0·3108	0·3097	20·8	21·0
			Average = 18·8.	

$\phi_0 = 0·3216$; $\pi_0 = 0·4113$; π_0 (corr.) = 0·3857.

It has already been pointed out that the velocity coefficient increases with the hydrogen-ion concentration, but not in direct proportion. If, however, the velocity coefficients of the reactions are compared in solutions of the same chloride-ion concentration, but different hydrogen-ion concentration, the velocity coefficients are nearly proportional to the square roots of the acidities. Thus, for azo–hydrazotoluidine at 18° with 0·1*N*-HCl + 0·1*N*-KCl and 0·2*N*-HCl as solvents, we have from Table XII

$$\sqrt{0·192/0·092} : 111/73 = 1·45 : 1·52,$$

and similarly, for azo- and hydrazo-aniline at 37° with 0·1*N*-HCl + 0·5*N*-KCl and 0·6*N*-HCl as solvents, we have from Table XIII

$$\sqrt{0·591/0·091} : 615/290 = 2·54 : 2·11.$$

Here the agreement is not so good, but, comparing the values of k for 0·1*N*-HCl and (0·1*N*-HCl, 0·5*N*-KCl), it seems probable that the discrepancy between the ratios may be due to a specific influence of the potassium chloride on the velocity of the reaction.

Finally, from a comparison of the mean value for k in Table XIII ($28·2 \times 10^{-5}$) and its value for the same solvent and temperature in Table XIV ($18·8 \times 10^{-5}$), it appears that the azo-compound also exerts a certain influence on the velocity, a property which is shared by many other unsaturated compounds.

EXPERIMENTAL.

Preparation of the Electrode Materials.—*3 : 3′-Diaminoazobenzene*, m. p. 155°, was prepared by Elbs's method ("Elektrolytische Darstellung Chemische Präparate," Halle, 1911, p. 107) by the electrolytic hydrogenation of *m*-nitroaniline, and was purified by treatment with concentrated sulphuric acid followed by crystallisation from alcohol.

3 : 3′-*Diamino*-4 : 4′-*dimethylazobenzene* was prepared in the same way from 4-nitro-3-aminotoluene. The crude azo-compound was then reduced to the hydrazo-compound (*vide infra*) and this was oxidised in hot alcoholic solution by means of a current of air or oxygen. M. p. 214° (corr.).

3 : 3′-*Diaminohydrazobenzene* was prepared by the electrolytic reduction of the corresponding azo-compound. Its purity was determined by addition of excess of 0·1*N*-iodine to a solution of 0·1199 gm. in acetone-free methyl alcohol, and back titration with thiosulphate (Required 11·24 c.c. Calc., 11·20 c.c.).

3 : 3′-*Diamino*-4 : 4′-*dimethylhydrazobenzene* also was prepared by electrolytic reduction. The azo-compound (9 gms.) was dissolved with 3 gms. of sodium acetate in 300 c.c. of 96 per cent. alcohol and 30 c.c. of water to form the cathode solution, and a saturated solution of sodium carbonate was employed in the anode compartment. The electrolysis was conducted with a platinum gauze cathode covered with an electrolytic deposit of lead. The area of the cathode was 55 sq. cm., and the current strength was 3·4—3·5 amperes for 1 hour 45 min. During the first 75 minutes the solution was kept boiling, and was then allowed to cool slowly to 15° for the remaining 30. The hydrazo-compound began to crystallise at about 38°. The crude product was filtered in an atmosphere of carbon dioxide, washed with water saturated with carbon dioxide, then with alcohol and ether, and was finally dried in a desiccator filled with carbon dioxide. It was purified by crystallisation from hot alcohol (6·5 gms. in 250 c.c.), and was filtered, washed with ether, and dried as before. The crystallisation was very slow. The yield was 40—50 per cent. of theory, and the freshly prepared product was snow white. It was analysed in the same way as hydrazoaniline and found to contain 98·62—98·78 per cent. of hydrazotoluidine, indicating possibly that superficial oxidation had occurred. The content of hydrazo- and azotoluidine was allowed for in the preparation of the solutions.

Preparation of the Electrode Solutions.—The solutions were prepared in the electrode vessels themselves with special precautions to avoid oxidation. The vessels used were of the type described by Biilmann (*Trans. Faraday Soc., loc. cit.*) and were of 150—250 c.c. capacity. The use of these large volumes was necessary on account of the sparingly soluble nature of the compounds employed, and, moreover, possesses the advantage that it reduces to a minimum the effect of the slight unavoidable oxidation.

A measured amount of solvent and an accurately weighed quantity of azo-compound were brought into the vessel, which was then stoppered and immersed in a thermostat. Solution was

effected by agitation with a stream of carbon dioxide which had been washed through the solvent employed and also served to remove air from the electrode vessel and the solution. Then the requisite quantity of the hydrazo-compound was rapidly added, the neck of the vessel was rinsed with 2 c.c. of the solvent, and the carbon dioxide agitation continued until solution was complete. The electrode was then fitted into position and the siphon tube filled by pressure of carbon dioxide.

The quinhydrone electrode was similar, but had only one-third the volume, and was fitted with three platinum electrodes. The connecting vessel was of glass, and contained the solvent electrolyte.

The electrodes employed were generally of bright platinum, about 3 sq. cm. in area. Bright, new, pure platinum is most satisfactory, and it is necessary to exercise care to avoid poisoning the electrode in welding it to the platinum wire lead. Gilded electrodes, both bright and covered with platinum black, were also employed in some cases, but it was found impossible to ensure satisfactory results with these electrodes. It was found that the azo–hydrazo electrode is very easily polarised. This is possibly due to the velocity of the reduction reaction, and is less at high than at low temperatures.

Measurement of Electromotive Force.—The *E.M.F.* measurements were carried out by means of a mirror galvanometer and a Wolff compensator. Because of the high velocity of inversion of hydrazotoluidine, it was found best to adjust the potential reading on the compensator to a definite value and to determine the time when no current passed the galvanometer. This time could be estimated with an accuracy of ± 3 seconds. The variation of potential with time was linear, but some of the earlier measurements showed discrepancies due possibly to temperature changes occurring during the process of solution, and some of the measurements near the end of the inversion showed discrepancies which may have been due to the fact that the concentration of hydrazo-compound was then very small. These discrepant results were not used in the calculations.

Summary.

1. It is shown that the affinity of an azo-compound for hydrogen may be determined electrometrically by measurement of the reduction potential of a solution containing the azo- and hydrazo-compound.

2. The potential of the azo–hydrazo electrode depends on the proportion of azo-compound to hydrazo-compound, so that the velocity coefficient of the rearrangement of the hydrazo-compound into a semidine or a benzidine may be determined by measuring

the change of potential of the azo–hydrazo electrode due to this rearrangement.

3. The reduction potentials and velocity coefficients were determined for azotoluidine and azoaniline under different conditions of temperature and hydrogen-ion concentration.

THE UNIVERSITY, COPENHAGEN. [*Received, May 5th*, 1924.]

CCXXIV.—*Researches on Residual Affinity and Co-ordination. Part XX. Chromic and Cobaltic Lakes of Mordant Azo-dyes.*

By GILBERT T. MORGAN and J. D. MAIN SMITH.

IT has been shown by our earlier researches that certain typical mordant dyes owe their power of forming lakes to the possession of univalent chelate groups each of which constitutes two units in the co-ordination complex of the coloured lake. These chelate groups are detected by the use of a suitable cobaltammine, which reacts with them with loss of ammonia; they are thus distinguished from any other acidic groups contained in the molecule (such as hydroxylic, carboxylic, and sulphonic radicals) by the fact that with the latter the cobaltammine forms salts without losing ammonia.

Every acidic mordant dye so far examined by this method has been found to contain at least one chelate group, the three typical classes being:—I, the quinoneoxime dyes, including dinitroso-resorcinol and the nitrosonaphthols (J., 1921, **119**, 704; 1922, **121**, 2857); II, the alizarin series, including alizarin red, orange and blue (J., 1922, **121**, 160); III, the azo-salicylato-group, including the so-called alizarin yellow 2G (J., 1922, **121**, 2866).

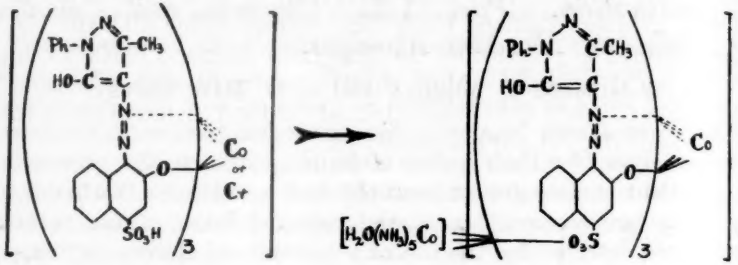
We have since extended this investigation to other classes of acidic mordant dyes, especially those in which the azo-chromophor is not remote from the chelate group as it is in the azo-salicylato-dyes. Three ortho-dihydroxyazo-dyes have now been examined:—eriochrome red B, Palatine chrome black 6B, and diamond black PV, and comparative experiments have been made on the ortho-aminohydroxyazo-dye, metachrome brown B. All these dyes have outstanding lake-producing properties and possess the same general configuration; the two auxochromic groups are on opposite sides of the azo-chromophor, so that if both auxochromic groups are implicated in the metallic lake a nine-membered ring would result.

The evidence derived from eriochrome red B,

$$\begin{matrix} \mathrm{N} & \mathrm{Ph{\cdot}C(OH)} \\ \| & \\ \mathrm{N} & \mathrm{CMe} \end{matrix} \!\!>\!\! \mathrm{C{\cdot}N_2{\cdot}C_{10}H_5(OH){\cdot}SO_3H},$$

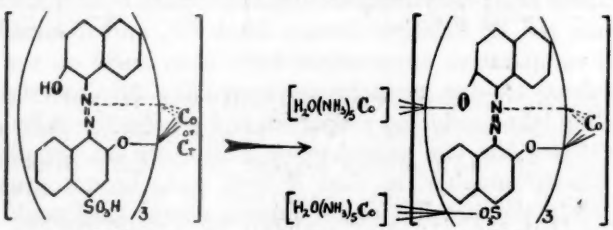
shows, however, that this colouring matter contains one chelate group and two salt-forming radicals, one being strongly and the other only feebly acidic. By the use of roseocobaltic chloride and its hydroxide (hydroxopentamminocobaltic hydroxide) three stages have been distinguished corresponding with the chelated cobaltic lake (I) and the mono-roseo (II) and diroseo-salt (III) of this lake. The corresponding chromic lake, also represented by formula I, is produced by the interaction of eriochrome red B and chromic fluoride in ammoniacal solution.

(I.) (II.)



(III.)

Palatine chrome black 6B, $HO{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_5(OH){\cdot}SO_3H$, when treated with roseocobaltic chloride, gives its simple cobaltic lake (IV)



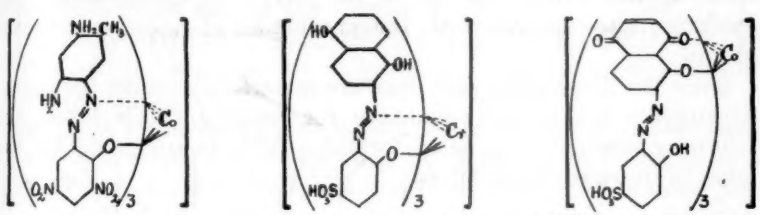
(IV.) (V.)

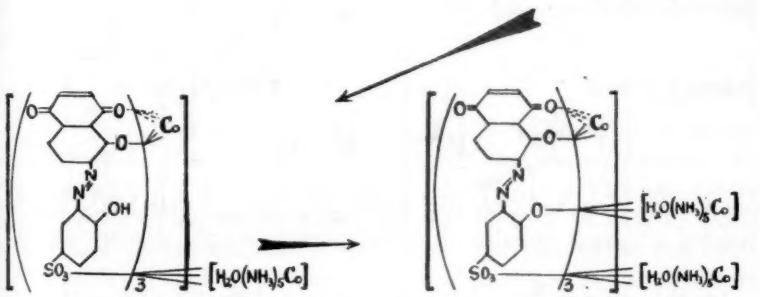
and with chromic fluoride the ammonium salt of the dye furnishes a chromic lake, also represented by formula IV. With excess of

roseocobaltic hydroxide, Palatine chrome black gives rise to the diroseo-salt (V) of the foregoing cobaltic lake.

The case of diamond black PV, $SO_3H{\cdot}C_6H_3(OH){\cdot}N_2{\cdot}C_{10}H_5(OH)_2$, presents exceptional features which elucidate the difficulties experienced in obtaining cobaltic lakes of oxidisable mordant dyes. Comparative experiments with chromic fluoride and roseocobaltic chloride show that only in the former combination is it possible to obtain a lake (VII) derived from the original colouring matter. In the interaction with roseocobaltic chloride oxidation occurs and although a simple cobaltic lake (VIII) can be isolated, it is a derivative of oxidised diamond black, thus corresponding with the black lake obtained in practice on the fibre from diamond black PV and chromic acid mordant. More drastic treatment with roseocobalt hydroxide converts the cobaltic lake of oxidised diamond black into monoroseo- (IX) and diroseo-salts (X):

(VI.) (VII.) (VIII.)





(IX.) (X.)

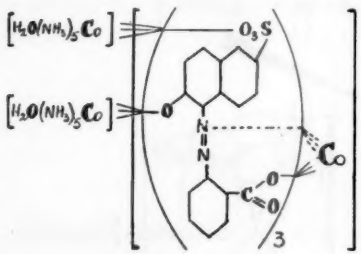
Metachrome brown B, $(NO_2)_2C_6H_2(OH){\cdot}N_2{\cdot}C_7H_5(NH_2)_2$, furnishes only the simple cobaltic lake (VI). It was, however, observed that with excess of cobaltammine reagent an unstable dicobaltic salt was obtained which rapidly decomposed on warming. This result indicates that the dye may undergo tautomeric change so that the amino-group becomes an imino-group with a feebly acidic hydrogen.

Tautomeric Form of Di-o-hydroxyazo-dyes.

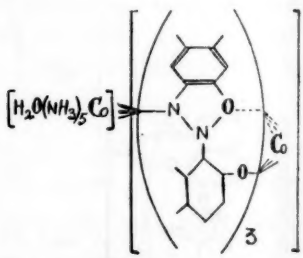
The foregoing formulations for the lakes and roseo-salts derived from di-*o*-hydroxyazo-dyes suggest that one hydroxyl group is not implicated in the chelate group and therefore is not essential to the production of these lakes. Hence the mono-*o*-hydroxyazo-dyes should also be capable of yielding lakes, but it was found that in many cases the property of lake-formation was too feeble to be detected by the cobaltammine reagents.

The interesting example of Fast red C (Carmoisine AS), $HSO_3 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_5(OH) \cdot SO_3H$, was examined. This mono-hydroxyazo-dye gives red shades on wool which are converted into blue by treatment with chromic acid, although the original colour remains unchanged with chromic salts. This difference points to oxidation as a concomitant reaction. When the dye is treated with roseocobaltic chloride, a complex tricobaltic lake is obtained with approximately the ratio $Co : NH_3 = 3 : 8$, suggesting that oxidation has occurred with the production of another hydroxyl group.

Since the di-*o*-hydroxyazo-dyes are remarkably unlike the mono-hydroxyazo-dye in their capacity for forming stable lakes, the following alternative general formula (XII) is suggested for the lakes of di-*o*-hydroxyazo-dyes:



(XI.)



(XII.)

In this tautomeric configuration the second hydroxylic group becomes implicated by migration of its hydrogen to one of the azo-nitrogen atoms, thus forming a feebly acidic (NH —) radical which may be present in the foregoing series of diroseo-salts.

Another explanation of the increased stability of the lakes of dihydroxyazo-dyes as affected by the presence of the second hydroxyl group is based on the analogy with alizarin and naphthazarin, in which dyes the second (β-) hydroxyl group increases very considerably the lake-forming power of the hydroxyl group contiguous to the chromophor (Kostanecki's rule).

[With HERBERT MUGGLETON STANLEY.]

It was previously shown (Morgan and Moss, *J. Soc. Chem. Ind*, 1923, **42**, 466) that the acetophenone-azo-β-naphthol-6-sulphonic acids had no mordanting properties, whereas *o*-carboxybenzeneazo-β-naphthol-6-sulphonic acid is a mordant dye. This lake-forming capacity is due to the *o*-carboxyl group present in the last-named colouring matter as shown by its reaction with roseocobalt hydroxide. The first product is a triroseocobalt salt, converted by heating into the lake (XI).

The latter substance is, however, not very stable and on continued boiling with ammonia is converted into a more soluble compound containing bivalent cobalt. This instability may be attributed to the seven-membered ring involving the metallic atom.

With the ortho- and meta-azo-compounds of acetophenone there is no evidence of normal lake-formation, but in the cold, acetophenone-*m*-azo-β-naphthol-6-sulphonic acid yields the triammonium monoroseo-cobalt salt of the dibasic dye acid,

$$[Co(NH_3)_5H_2O]'''\{SO_3{\cdot}C_{10}H_5(O{\cdot}NH_4){\cdot}N_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH_3\}_3$$

(XIII), which loses ammonia on keeping owing to the feeble acidity of the phenolic group.

Although the cobaltammine lakes described above are of the roseo-cobalt type $[H_2O(NH_3)_5Co]X$, they correspond with the purpureo-lakes of our earlier researches (*loc. cit.*) in containing the same proportions of cobalt (n) and ammonia (m) as required by the equation $m = 5(n - 1)$, which has now been found to be general for six types of acidic mordant dyes.

EXPERIMENTAL.

1. *Chromic Lake of Eriochrome Red B* (*G*), (2-*Chromic* 4-*Sulpho*-β-*naphthoxide*-1 : 4′-*azo*-1′-*phenyl*-3′-*methyl*-5′-*pyrazolone*, formula I). *Preparation*:—7·5 C.c. of 2*N*-chromic fluoride (= 0·26 gm. Cr or 50 per cent. excess) were warmed with 4·24 gms. of eriochrome red B in 30 c.c. of 2*N*-ammonia for 15 minutes. The precipitate was twice extracted with boiling 2*N*-ammonia, and the cooled filtrates were acidified with 6*N*-hydrochloric acid (yield 82 per cent.).

The substance is a carmine red lake with green reflex. It forms bright red, aqueous solutions, brownish-red solutions with ammonia or pyridine, and intense orange solutions with aqueous or alcoholic soda. The dyeing on wool is cardinal red. Concentrated sulphuric acid and methyl sulphate give magenta and scarlet colorations [Found: Cr = 3·82. $(C_{20}H_{15}O_5N_4S)_3Cr$ requires Cr = 3·94 per cent.].

2. *Cobaltic Lakes of Eriochrome Red B* (2-*Cobaltic* 4-*Sulpho*-β-*naphthoxide*-1 : 4′-*azo*-1′-*phenyl*-3′-*methyl*-5′*pyrazolone*, *nona- and*

tri-hydrates, formula I). *Preparation*:—Roseocobaltic chloride (0·7 gm.) in 20 c.c. of 3*N*-ammonia was added to 3·18 gms. of eriochrome red B in 20 c.c. of 3*N*-ammonia; the solution was boiled for 15 minutes, cooled, and acidified with 2*N*-hydrochloric acid, and the lake reprecipitated from 3*N*-ammonia (yield 96 per cent.).

The compound is a dark red powder with green reflex; its solutions in water, ammonia, or aqueous sodium hydroxide are brownish-red, and it dyes wool in brownish-red shades. Alcoholic soda, pyridine, methyl sulphate, and strong sulphuric acid gave red, crimson, orange, and brown to magenta colorations [Found: Co = 3·93; H_2O = 10·84. $(C_{20}H_{15}O_5N_4S)_3Co(H_2O)_9$ requires Co = 3·96; H_2O = 10·87. Found: in material dried over calcium chloride, Co = 4·2; N = 11·7; S = 6·50. $(C_{20}H_{15}O_5N_4S)_3Co(H_2O)_3$ requires Co = 4·2; N = 12·1; S = 6·94 per cent.].

3. *Roseocobaltic Salt of Cobaltic Lake of Eriochrome Red B* (4-*Aquopentamminocobaltic* 2-*Cobaltic* 4-*Sulphonato*-β-*naphthoxide*-1:4′-*azo*-1′-*phenyl*-3′-*methyl*-5′-*pyrazolone*, formula II). *Preparation*:—Eriochrome red B (2·55 gms.) was added to the red solution prepared from 1·075 gms. of roseocobaltic chloride, 10 c.c. of water, and excess of silver oxide. The dark yellow solution changed to reddish-brown with evolution of ammonia and set to a glistening, silky, brown paste, which was washed with alcohol and ether (yield 70 per cent.).

The substance is a brown salt with green reflex, sparingly soluble in water, ammonia, or cold caustic soda. Its colour reactions are those recorded for the cobaltic lake [Found: Cr = 7·6; NH_3 = 5·7. $(C_{20}H_{14}O_5N_4S)_3Co_2(NH_3)_5,H_2O$ requires Co = 7·9; NH_3 = 5·7 per cent.].

4. *Diroseocobaltic Salt of Cobaltic Lake of Eriochrome Red B* (formula III). *Preparation*:—Eriochrome red B (3·2 gms.) was added to 3 gms. of roseocobaltic oxalate and 95 c.c. of *N*/4-barium hydroxide; the reddish-brown filtrate yielded a brown precipitate, with evolution of ammonia, which was washed with water, alcohol, and ether (yield 60 per cent.).

The brown powder gives similar colorations to the two preceding compounds [Found: Co = 11·2; NH_3 = 9·5.

$$(C_{20}H_{13}O_5N_4S)_3Co_3(NH_3)_{10}(H_2O)_2$$

requires Co = 10·8; NH_3 = 10·3 per cent.].

5. *Chromic Lake of Palatine Chrome Black 6B* [B], *Eriochrome Blue Black R* [G], *Salicin Black V* [K], (2-*Chromic* 4-*Sulpho*-β-*naphthoxide*-1 : 4′-*azo*-β-*naphthol trihydrate*, formula IV).—The dark purple lake prepared by the chromic fluoride method (p. 1735, No. 1) (yield 32 per cent.), gave purple solutions in water or hot aqueous or

alcoholic sodium hydroxide, and violet solutions with ammonia, pyridine, methyl sulphate, or strong sulphuric acid; and a purple dyeing on wool [Found: Cr = 4·14; N = 6·59; H_2O = 4·22; eqt. wt. = 438·5. $(C_{20}H_{13}O_5N_2S)_3Cr(H_2O)_3$ requires Cr = 4·05; N = 6·54; H_2O = 4·20 per cent.; eqt. wt. = 428·3].

6. *Cobaltic Lake of Palatine Chrome Black 6B* (*2-Cobaltic 4-Sulpho-β-naphthoxide-1 : 1′-azo-β-naphthol trihydrate*, formula IV).—Prepared with roseocobaltic chloride (p. 1736, No. 2) (yield 87 per cent.) this substance gave a dark violet dyeing on wool, violet solutions in water, ammonia, pyridine, and aqueous or alcoholic soda, and dark blue colorations with methyl sulphate or strong sulphuric acid [Found: Co = 4·51; H_2O = 8·06. $(C_{20}H_{13}O_5N_2S)_3Co(H_2O)_6$ requires Co = 4·38; H_2O = 8·02 per cent.].

A similar preparation with twice as much roseocobaltic chloride and neutralised only with dilute hydrochloric acid gave an unstable mono-roseo salt changing to the monocobaltic lake.

7. *Diroseocobaltic Salt of Cobaltic Lake of Palatine Chrome Black 6B* (*Bisaquopentamminocobaltic 2-cobaltic 4-sulphonato-β-naphthoxide-1 : 1′-azo-β-naphthoxide*, formula V) was prepared by the silver oxide method as on p. 1736, No. 3 (yield quantitative). It is insoluble in water or 6*N*-ammonia, dissolves in warm 5*N*-sodium hydroxide to a purple solution, evolving ammonia. The solution in pyridine is purple, but the other colour reactions are similar to those of the preceding lake [Found: Co = 11·4; NH_3 = 9·8. $(C_{20}H_{11}O_5N_2S)_3Co_3(NH_3)_{10}(H_2O)_2$ requires Co = 11·4; NH_3 = 10·9 per cent.].

8. *Cobaltic Lake of Metachrome Brown B* [A], (*1-Cobaltic 4 : 6-dinitrophenoxide-2-azo-m-tolylenediamine*, formula VI) was prepared by the roseocobalt chloride method of p. 1736, No. 2 (yield 94 per cent.). The black lake gives a purple streak on paper, is insoluble in water, ammonia, or pyridine, but dissolves sparingly in warm 5*N*-sodium hydroxide to a greenish-brown solution. It has no dyeing properties, and gives reddish-violet colorations with methyl sulphate and strong sulphuric acid [Found: Co = 5·9; N = 23·7. $(C_{13}H_{11}O_5N_6)_3Co$ requires Co = 5·6; N = 24·0 per cent.].

9. *Chromic Lake of Diamond Black PV* [By], (*1-Chromic 4-sulphophenoxide-2 : 2′-azo-1′ : 5′-dihydroxynaphthalene trihydrate*, formula VII) was prepared by the chromic fluoride method of p. 1735, No. 1 (yield 40 per cent.). After heating for 6 hours at 105°, the purple lake turned black with gain in weight, owing to oxidation. The unoxidised lake gave a dark purple dyeing (3 per cent.) on unmordanted wool, but with chromic acid mordant a black shade. Its solutions in water or aqueous sodium hydroxide are magenta

red, and in ammonia or aqueous pyridine, blue. The colorations with methyl sulphate and strong sulphuric acid are dark green and purple like those of diamond black [Found: Cr = 4·22; N = 7·01; H_2O = 4·19. $(C_{16}H_{11}O_6N_2S)_3Cr(H_2O)_3$ requires Cr = 4·39; N = 7·09; H_2O = 4·56 per cent.].

10. *Cobaltic Lake of Oxidised Diamond Black PV* (formula VIII). *Preparation*:—Roseocobaltic chloride (1·34 gms.) in 40 c.c. of water was added to 5·73 gms. of purified diamond black PV (sodium salt) in 500 c.c. of water. The solution set to a dark red jelly of the roseo-salt of the dye, which rapidly decomposed with evolution of ammonia; the clear violet solution of the cobaltic lake became dark purple after 1 hour. The oxidised solution was acidified with 2*N*-hydrochloric acid, and the purple-black precipitate washed with hydrochloric acid (yield 32 per cent.).

This lake of oxidised diamond black was almost insoluble in water and had little affinity for wool, giving only pale greyish-black tints, whereas the preceding unoxidised chromic lake was soluble to a violet-red solution and dyed wool in purple shades changed to black by chromic acid mordant. The oxidised cobaltic lake dissolved in 6*N*-ammonia, pyridine, 5*N*-aqueous or alcoholic soda to purple-black solutions, was insoluble in methyl sulphate, and gave a dead black coloration with strong sulphuric acid, becoming purple on dilution [Found: Co = 4·89; N = 6·98; H_2O = 4·79. $(C_{16}H_9O_7N_2S)_3Co(H_2O)_3$ requires Co = 4·79; N = 6·82; H_2O = 4·38 per cent.].

11. *Roseocobaltic Salt of the Cobaltic Lake of Oxidised Diamond Black PV* (formula IX). *Preparation*:—The general method with silver oxide (p. 1736, No. 3) was employed (yield 80 per cent.). This dicobaltic lake of oxidised diamond black was sparingly soluble in water and resembled the preceding monocobaltic lake in its colour reactions and in its lack of affinity for wool [Found: Co = 9·23; NH_3 = 6·37; azo-N_2 = 5·28. $(C_{16}H_8O_7N_2S)_3Co_2(NH_3)_5,H_2O$ requires Co = 8·82; NH_3 = 6·36; azo-N_2 = 6·28 per cent.].

12. *Diroseocobaltic Salt of the Cobaltic Lake of Oxidised Diamond Black PV* (formula X). *Preparation*:—By the general method with silver oxide (p. 1736, No. 3); yield 77 per cent. The tricobaltic lake slowly evolved ammonia, leaving 6·8 per cent. NH_3, the loss corresponding with the break up of one roseocobaltic complex. The salt is more sparingly soluble than the preceding dicobaltic compound but similar in its colour reactions and in lack of affinity for wool, this fibre being only dyed in pale greyish-black tints [Found: Co = 12·45; NH_3 = 10·44; azo-N_2 = 5·82.

$$(C_{16}H_7O_7N_2S)_3Co_3(NH_3)_{10}(H_2O)_2$$

requires Co = 11·83; NH_3 = 11·36; azo-N_2 = 5·62 per cent.].

[With HERBERT MUGGLETON STANLEY.]

13. *Diroseocobaltic Salt of the Cobaltic Lake of* o-*Carboxybenzeneazo*-β-*naphthol*-6-*sulphonic Acid* (formula XII). *Preparation* :—By the general method (p. 1736, No. 2); yield 26 per cent. This dark greenish-brown lake, insoluble in organic solvents, was sparingly soluble in water to a green solution and possessed no dyeing properties. On prolonged evaporation with aqueous ammonia, it was decomposed, yielding an extremely soluble purple solid which combined the properties of an ammonium salt and a cobaltammine salt of the dye acid [Found : Co = 12·1; NH_3 = 11·5; total N = 14·8.

$$(C_{17}H_9O_6N_2S)_3Co_3(NH_3)_{10},(H_2O)_2$$

requires Co = 11·9; NH_3 = 11·4; total N = 15·0 per cent.].

14. *Triammonium Monoroseocobaltic Salt of* m-*Acetylbenzeneazo*-β-*naphthol*-6-*sulphonic Acid* (formula XIII). *Preparation* :—A red precipitate separated from solutions of 0·45 gm. of purpureo-cobalt chloride in 1·5 c.c. of 6*N*-ammonia and 10 c.c. of water, and 1 gm. of *m*-acetylbenzeneazo-β-naphthol-6-sulphonic acid in 1 c.c. of 6*N*-ammonia and 90 c.c. of water (yield 60 per cent.).

This brick red salt gave a red aqueous solution and lost ammonia on keeping. The low analytical figures for NH_3 were due to loss in drying, as the ratio Co/NH_3 in the freshly prepared compound was 1 atom to 8 mols. [Found : Co = 5·05; NH_3 = 8·95.

$$(C_{18}H_{12}O_5N_2S)_3Co(NH_3)_5(NH_4)_3,H_2O$$

requires Co = 4·50; NH_3 = 10·3 per cent.].

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research for grants which have helped to defray the expense of this investigation.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

[*Received, April 3rd*, 1924.]

CCXXV.—*Studies in the Resolution of Racemic Acids by Optically Active Alcohols. Part III. The Resolution of* r-*Tartaric and* r-*Dimethoxysuccinic Acids by* l-*Menthol.*

By HENRY WREN and (MISS) KATHLEEN H. HUGHES.

SINCE, during recent years, the resolution of racemic acids by the crystallisation of their esters with optically active alcohols has been found to be more commonly possible than had been suspected previously (compare Wren and Wright, J., 1921, **119**, 798; McKenzie and Smith, J., 1923, **123**, 1962), it appeared desirable to extend the

observations to analogous cases with the object of ascertaining whether greater regularities are associated with this method of resolution than with that involving the use of alkaloids. It has been found that *r*-tartaric acid is readily resolvable by the fractional crystallisation of its *l*-menthyl hydrogen ester; in this instance, the ester derived from the *l*-acid is the more sparingly soluble of the diastereoisomerides, whereas with *l*-borneol (Wren, Williams, and Myddleton, J., 1920, **117**, 191) the reverse is the case. *r*-Dimethoxysuccinic acid may be resolved by crystallisation of the normal *l*-menthyl ester. In the case of *r*-tartaric acid the observed phenomena are due, beyond doubt, to resolution by fractional crystallisation, since the initial ester was prepared by admixture of equal quantities of the pure diastereoisomerides. With *r*-dimethoxysuccinic acid, a complication is involved, since the normal ester was prepared by the direct esterification of the *r*-acid with *l*-menthol; if the process is not carried quite to completion, the product should contain unequal amounts of *l*-menthyl *d*- and *l*-dimethoxysuccinates. In general, the rates of esterification of the enantiomorphous forms of racemic acids by optically active alcohols do not differ very widely from one another (compare Marckwald and McKenzie, *Ber.*, 1899, **32**, 2130; 1901, **34**, 469; McKenzie and co-workers, J., 1902, **81**, 1411; 1905, **85**, 380; 1915, **107**, 712), but systematic observations of this nature have not, up to the present, been extended to dibasic acids. In these cases, the conditions are not quite comparable, since enantiomorphism is here confined to the production of the hydrogen ester, the subsequent conversion of the latter into the normal esters taking place from compounds which are no longer mirror images of one another (compare Wren and Still, J., 1917, **111**, 513). It appears, however, justifiable to conclude that resolution in this case is due essentially to crystallisation, since it has been possible to obtain both active acids, whereas, if the isolation of the ester of one active form had been due to its excessive production, the remaining ester would have been derived from the racemic acid.

EXPERIMENTAL.

Resolution of r-*Tartaric Acid by Crystallisation of its* l-*Menthyl Hydrogen Ester.*—The normal *l*-menthyl *d*- and *l*-tartrates were prepared by Patterson and Kaye's method (J., 1905, **87**, 33, 122; 1906, **89**, 1884); in the case of the *l*-ester the initial material was potassium hydrogen *l*-tartrate. They are readily converted into the corresponding hydrogen esters by half-hydrolysis with boiling, aqueous-alcoholic potassium hydroxide (compare Wren, Williams, and Myddleton, *loc. cit.*).

l-*Menthyl hydrogen* d-*tartrate*, aggregates of radiating needles, from light petroleum, melts at 82·5—83° (Found: C = 58·1; H = 8·2. Calc., C = 58·3; H = 8·4 per cent.). In chloroform solution: $l = 2$, $c = 2·856$, $\alpha_D^{17·6°}$ −3·03°, $[\alpha]_D^{17·6°}$ −53·04°.

l-*Menthyl hydrogen* l-*tartrate*, short, colourless needles, from light petroleum (b. p. 60—80°)–benzene (equal vols.), melts at 122—122·5° (Found: C = 58·6; H = 8·5. Calc., C = 58·3; H = 8·4 per cent.). In chloroform: $l=2$, $c=2·8428$, $\alpha_D^{21·4°}$ −4·04°, $[\alpha]_D^{21·4°}$ −71·06°.

The absence of racemisation during hydrolysis is proved by the identity of the *l*-menthyl hydrogen esters obtained in this manner with those isolated in small amounts from the products of the direct esterification of the acids.

A solution of *l*-menthyl hydrogen *d*- and *l*-tartrates (20 gms. of each) in boiling benzene (40 c.c.)–light petroleum (250 c.c.) was allowed to cool. After 3 days, the crystalline crop (13·7 gms.) was removed; it had m. p. 117—119°, $[\alpha]_D^{18·2°}$ −69·06° in chloroform. After hydrolysis by aqueous-alcoholic potassium hydroxide, removal of alcohol and menthol, addition of hydrochloric acid in amount required for the formation of the potassium hydrogen salt, the product, after being crystallised from water, was pure potassium hydrogen *l*-tartrate (Found: K = 20·8. Calc., K = 20·7 per cent.). 0·6000 Gm. neutralised 32·0 c.c. of *N*/10-potassium hydroxide; calc., 31·93 c.c. 2·0104 Gms. were neutralised with potassium hydroxide and the solution made up to 25 c.c. with water; the solution had $\alpha_D^{14·5°}$ −5·34° ($l = 2$), whence $[\alpha]_D^{14·5°}$ −27·63°, whereas Schütt (*Ber.*, 1888, **21**, 2586) found for normal potassium *d*-tartrate $[\alpha]_D^{20°}$ + 28·01° ($c = 9·62$).

The filtrate from the somewhat impure *l*-menthyl hydrogen *l*-tartrate was evaporated to dryness and the residue hydrolysed. The mixture of potassium *d*- and *r*-tartrates was converted through the calcium salts into the corresponding free acids, from which the bulk of the racemic compound was removed by cautious crystallisation from water. The remaining acid was transformed into the potassium hydrogen salt, from which pure potassium hydrogen *d*-tartrate was isolated by repeated crystallisation from water (Found: K = 20·3. Calc., K = 20·7 per cent.). 1·6188 Gms., neutralised with potassium hydroxide and made up with water to 25 c.c., had $\alpha_D^{18·4°}$ + 4·33° ($l = 2$), whence $[\alpha]_D^{18·4°}$ + 27·81° for the normal salt.

Distinct evidence of the resolution of *l*-menthyl hydrogen *r*-tartrate from solution in carbon disulphide and carbon tetrachloride was obtained, these being the only other solvents from which crystals were readily deposited. Thus, when a solution of 2 gms. of the ester in boiling carbon disulphide (15 c.c.) was allowed to

cool, a crystalline crop separated which had $[\alpha]_D^{16\cdot4^\circ} - 67\cdot84^\circ$, whereas the material recovered from the filtrate had $[\alpha]_D^{17\cdot4^\circ} - 57\cdot8^\circ$. The crystals which separated slowly from a solution of the ester (2 gms.) in carbon tetrachloride (10 c.c.) had $[\alpha]_D^{19\cdot4^\circ} - 63\cdot5^\circ$ in chloroform.

Resolution of r-*Dimethoxysuccinic Acid by* l-*Menthol.*—*r*-Dimethoxysuccinic acid is conveniently prepared by the hydrolysis of ethyl *r*-dimethoxysuccinate with a small excess of boiling, aqueous barium hydroxide solution, precipitation of excess of alkali by carbon dioxide, filtration, and evaporation of the filtrate to dryness. The residual barium salt is dried at 105°, dissolved in water, and decomposed with the requisite quantity of sulphuric acid.

r-*Dimethoxysuccinic acid* separates from water, in which it is more sparingly soluble than the corresponding optically active acids, in colourless rhombs containing $2H_2O$. The anhydrous acid melts somewhat indefinitely at 168—171° (Found: $H_2O = 16\cdot6$. $C_6H_{10}O_6,2H_2O$ requires $H_2O = 16\cdot8$ per cent. Found: $C = 40\cdot6$; $H = 5\cdot1$. $C_6H_{10}O_6$ requires $C = 40\cdot4$; $H = 5\cdot0$ per cent.).

Di-*l*-menthyl *r*-dimethoxysuccinate was obtained by heating dehydrated *r*-dimethoxysuccinic acid with three times its weight of *l*-menthol for 20 hours at 120° in an intermittent current of dry hydrogen chloride or, more conveniently, by the action of *l*-menthol on ethyl *r*-dimethoxysuccinate under similar conditions during 30 hours. The product, dissolved in ether, was shaken with water and sodium carbonate solution to remove unchanged acid and hydrogen ester, and the menthol was distilled in steam. The normal ester, which was isolated in the usual manner and solidified readily ($[\alpha]_D^{21^\circ} - 68\cdot8^\circ$ in chloroform), was repeatedly crystallised from ethyl alcohol, whereby ultimately *di*-l-*menthyl* l-*dimethoxysuccinate* was isolated. It crystallised in long, radiating needles, m. p. 88·5—89·5° (Found: $C = 68\cdot4$; $H = 9\cdot8$. $C_{26}H_{46}O_6$ requires $C = 68\cdot7$; $H = 9\cdot9$ per cent.). In chloroform: $l = 2$, $c = 2\cdot138$, $\alpha_D^{18\cdot8^\circ} - 4\cdot95^\circ$, $[\alpha]_D^{18\cdot8^\circ} - 115\cdot1^\circ$; in benzene: $l = 2$, $c = 2\cdot1456$, $\alpha_D^{16\cdot4^\circ} - 5\cdot21^\circ$, $[\alpha]_D^{16\cdot4^\circ} - 121\cdot4^\circ$; in ethyl alcohol: $l = 2$, $c = 2\cdot0908$, $\alpha_D^{16\cdot8^\circ} - 4\cdot95^\circ$, $[\alpha]_D^{16\cdot8^\circ} - 118\cdot4^\circ$. The identity of the ester was established by direct comparison with the product of the action of *l*-menthol on ethyl *l*-dimethoxysuccinate and also by its hydrolysis to *barium* l-*dimethoxysuccinate*; the salt crystallises from water with approximately $5H_2O$ (Found: for the anhydrous salt, $Ba = 43\cdot4$. Calc., $Ba = 43\cdot7$ per cent.). In water: $l = 2$, $c = 0\cdot950$, $\alpha_D - 0\cdot48^\circ$, $[\alpha]_D - 25\cdot2^\circ$. For barium *d*-dimethoxysuccinate Purdie and Irvine (J., 1901, **79**, 959) record the value, $[\alpha]_D^{20^\circ} + 27\cdot22^\circ$ for $c = 1\cdot3775$.

The ester remaining in solution after the first crystallisation of the di-*l*-menthyl *dl*-dimethoxysuccinate was hydrolysed with barium hydroxide and the mixture of barium salts was converted into the

corresponding acids, which were found to be strongly dextrorotatory in aqueous solution; the isolation of the homogeneous *d*-acid could not, however, be effected.

The authors have pleasure in expressing their gratitude to the Research Fund Committee of the Royal Society for a grant which has defrayed a part of the expenses of the investigation.

MUNICIPAL COLLEGE OF TECHNOLOGY,
BELFAST. [*Received, June 13th,* 1924.]

CCXXVI.—*Tesla-luminescence Spectra. Part IV. Some Hydrocarbons containing a Single Benzene Nucleus.*

By WILLIAM HAMILTON MCVICKER, JOSEPH KENNETH MARSH, and ALFRED WALTER STEWART.

IN previous papers (J., 1923, **123**, 642, 817, 2147), an examination was made of the spectra emitted under the influence of the Tesla discharge by the vapours of benzene and a number of its mono-substitution products. In the present communication, this work is extended to embrace the disubstituted hydrocarbon derivatives of benzene, both open-chain and cyclic; and the spectra of styrene and phenylacetylene have been included also: so that fairly extensive material is now available, dealing with the influence of unsaturation, ring-formation, and position-isomerism upon these spectra.

1. *Apparatus.*—Two modifications have been made in the apparatus previously described. A new Tesla transformer has been brought into use, supplied by the Medical Supply Association, Ltd. It is air-insulated; and its secondary is directly coupled to its primary: the total number of its coils is 70; and the primary is variable up to 24 coils. There are two Leyden jars, each of about a litre capacity; and the transformer is actuated by a 12-inch induction coil with a motor contact-breaker.

This exchange of one transformer for another produces no measurable alteration in the character of the spectra, as we had already established; and further exhaustive tests made by us have confirmed our previous results in this matter.

Instead of the original glass cell with a quartz window, a new all-quartz cell is now employed. At one end of the axial tube of this cell an optically-worked quartz flat window is fused in. Just below this, a quartz bulb is blown on to the axial tube; and from

this bulb the substance under examination is vaporised into the cell. The vapour is kept in constant flow down the tube of the cell by means of a mercury pump attached to the far end of the tube; and the vacuum for the mercury pump is furnished by a motor-driven oil-pump. The internal electrode—a mercury-filled glass tube—projects into the cell immediately above and behind the quartz window. The external electrode is a piece of metal foil wrapped round the outside of the axial tube of the cell. The remainder of the arrangements are the same as those already described, except that a new slit has been fitted to the spectrograph.

The results obtained with various compounds are given below. The numbers are wave-lengths; and when a number is placed in brackets, this indicates that the corresponding band is very faint, so that the figure is not absolutely accurate. We have re-examined the spectra of toluene and ethylbenzene with the new slit, so as to make the whole series of substances comparable with one another, as the new slit has yielded sharper results than our older one.

2. *Toluene.*—B. p. 110°. Examined at 4—5 mm. pressure and at room temperature.

An intense continuous spectrum from 2602 to 3700. Heads of bands at (2602), (2613), 2629, 2635, 2667, 2671, 2680, 2688, 2693, (2701), 2705, 2713, 2718, 2725, 2732, 2742, 2755, 2771, 2786, 2804, 2820, 2834, 2866, (2905).

Also spectrum in the visible region which has no continuous background but contains heads of bands at 3980*, 4267*, 4474, 4605,* 4655,* 4670.*

3. *Ethylbenzene.*—B. p. 135—136·2°/754 mm. Examined at 4—5 mm. pressure and room temperature.

An intense continuous spectrum between 2660 and 3600 with diffuse bands with heads at 2660, 2666, (2678), (2688), 2706, 2718, 2736. Another band appears to lie about 2800.

The spectrum in the visible is identical with that of toluene.

4. o-*Xylene.*—B. p. 144·4—144·7°/769 mm. Examined at 1—2 mm. pressure and room temperature.

An intense spectrum between 2680 and 3500. Heads of bands at 2681, 2686, 2691, 2736, 2740.

Medium spectrum in visible between 4677 and 4980, with heads of bands at 3976,* 4270,* 4602,* 4677, 4791, 4846, 4980.

* Bands marked with an asterisk are apparently members of the series of so-called "Blue Bands" which are characteristic of the spectrum of benzaldehyde and appear also in the spectra of some benzene mono-substitution products.

5. m-*Xylene.*—B. p. 139·2—139·4°. Examined at 1—2 mm. pressure and room temperature.

An intense spectrum from 2673 to 3580, with heads of bands at 2673, 2705, 2712, 2719, 2724, 2730, 2744, 2750, 2761, 2765, 2781. Three very indistinct bands were traced at 2802, 2817, 2840.

Also very faint spectrum in the visible between 4659 and 4808, with heads at 4659 and 4769.

6. p-*Xylene.*—B. p. 138·4—138·7°/769 mm. Examined at 1—2 mm. pressure and at room temperature.

An intense continuous spectrum between 2675 and 3850, with heads at 2724, 2732, 2738, 2746, 2774, 2787, 2794, 2803, 2812, 2817, 2824, 2853, 2869, 2883, 2922, 2954.

Also in visible, a strong spectrum between 4535 and 5285, with heads of bands at 3952, 4250, 4310, 4535, 4614, 4703, 4765, 4805, and 4905.

7. *Mesitylene.*—B. p. 164·6—165·5°/769 mm. Examined at 1—2 mm. pressure and at a temperature sufficient to vaporise the substance.

A fairly intense spectrum between 2703 and 3800 with heads of bands at 2703, 2707, 2775, and 2781.

8. p-*Cymene.*—B. p. 177·0—177·4°/768 mm. Examined at 1—2 mm. pressure and room temperature.

A fairly intense spectrum between 2710 and 3500, with diffuse bands at 2710, 2771, (2804), (2839), (2871).

In the visible, a medium spectrum from 4670 to 5300, with the centre of a diffuse band at 4720.

9. *Indene.*—B. p. 179·0—180·4°. Examined at 1 mm. pressure and room temperature.

A fairly intense spectrum from 2780 to 3800, with bands at 2780, 2785, 2790, 2795, 2801, 2840, 2845, 2850, 2862, 2882, 2887, 2905, 2909, (2936), 2948, 2951, 2967.

In the visible, an intense spectrum from 4722 to 5670, with bands at 4722, 4860, 5015, and 5105.

10. *Hydrindene.*—B. p. 177—181°/771 mm. Examined at 2 mm. pressure and room temperature.

An intense spectrum from 2702 to 3700, with bands at 2702, 2710, 2721, 2767, 2772, 2779, 2789, and 2803.

In the visible, a very intense spectrum from 4584 to 5965, with bands at 4584, 4720, 4898, 5015, and 5105.

11. *Naphthalene.*—B. p. 217·4—217·8°/769 mm. Examined at 1—2 mm. pressure and at a temperature just sufficient to volatilise the compound.

A continuous spectrum fading off gradually at both ends and extending between 2800 and 5000, the region of maximum intensity

being from 3200 to 4000. Indistinct bands observed at 3082 and 3176.

12. *Tetrahydronaphthalene.*—B. p. 205°. Examined at 1—2 mm. pressure and at a temperature just sufficient to volatilise the substance.

A very intense continuous spectrum from 2719 to 4400, with diffuse bands at (2719), 2821, 2908, 3083—3103, 3179.

In the visible, an intense spectrum between 4572 and 6170 with heads of bands at 4572, 4677, 4825—4900, 5080.

13. *Hexaethylbenzene.*—M. p. 126·5°. Examined at 1—2 mm. pressure and at a temperature sufficient for volatilisation.

A very faint continuous spectrum between 3050 and 4200, fading off gradually at both ends.

14. *Styrene.*—B. p. 143·5—145·5°/745 mm. Examined at a pressure of 1·5 mm. and room temperature.

A fairly intense continuous spectrum from 2830 to 3900, with heads of bands at 2866, 2872, 2877, 2884, 2891, 2896, 2930, 2935, 2961, 2972, 2981, 3020.

15. *Phenylacetylene.*—B. p. 140—144°. Examined at 2 mm. pressure and room temperature.

A medium continuous spectrum from 2787 to 4100, with heads of bands at 2787, 2801, 2825, 2827, 2837, 2867, 2911, 2919, 3010.

In the visible, a faint spectrum with bands at 4314, 4478—4518, and 4672.

16. *General Characteristics of these Spectra.*

As a rule, in those spectra which show clearly banded structure, the end of shorter wave-length is abrupt, terminating in a well-defined band-head.* The group of bands to which this is the main head is, in general, not very intense. The group next to this (towards the red) is stronger, its head being brighter and well-defined. Thereafter, the intensity of the spectrum continues strong through a considerable range, including several band groups in some cases, and then gradually fades off as the wave-length increases. It may be recalled that the benzene spectrum itself answers to the same description.

It appears to be improbable that these spectra are simply fragments of the benzene spectrum shifted up towards the red region; for when corresponding bands in different groups are identified and the differences between them are ascertained, it is found that they differ considerably from each other and from the frequency-difference of approximately 100 units which separates the members

* In one or two cases there is a faint continuation of the spectrum beyond the band head.

of one band group of benzene from the corresponding members of adjacent groups. The figures below give the frequencies of comparable bands in various spectra, the differences being printed in italics. The numbers in the top line in each case are those of the heads of band groups.

Toluene:

3749	*80*	3669	*103*	3565	*101*	3465
3744	*84*	3660				
3731	*84*	3647	*101*	3546	*104*	3442

Ethylbenzene:

3759	*81*	3678	*107*	3571		

Styrene:

3475	*98*	3377	*66*	3311		
3467	*102*	3365				

Phenylacetylene:

3588	*51*	3537	*102*	3435		
		3525	*99*	3426	*104*	3322

o-*Xylene*:

3730	*75*	3655				
3723	*73*	3650				

m-*Xylene*:

3697	*75*	3622				
3671	*75*	3596				

p-*Xylene*:

3671	*83*	3588	*38*	3550	*45*	3505	*37*	3468	*45*	3423	*38*	3385
3660	*81*	3579	*38*	3541								

p-*Cymene*:

3690	*81*	3609				

Mesitylene:

3700	*97*	3603				
3695	*99*	3596				

Indene:

3597	*76*	3521	*51*	3470	*78*	3392		
3590	*75*	3515	*52*	3463				
3584	*75*	3509						

Naphthalene:

3245	*96*	3149				

Hydrindene:

3690	*76*	3614	*47*	3567		

Tetrahydronaphthalene:

3545	*96*	3439				

An examination of the relative intensities of the various spectra leads to interesting results. Benzene, toluene, the three xylenes, and ethylbenzene all yield intense spectra. When the substituent groups are still further increased in total mass—as in mesitylene and *p*-cymene—the spectra are less brilliant; and finally in the case of hexaethylbenzene the spectrum is quite faint. It therefore appears that in these hydrocarbons the weighting of the ring with substituent alkyl groups tends to damp down the process which gives rise to the Tesla-luminescence spectra. The fact that the quite symmetrically-substituted hexaethylbenzene has the feeblest spectrum of all is a proof that this fading-out is not entirely attributable to uneven loading of the ring. In view of the fact that the sharpest series of bands is found in benzene's spectrum, and since the number of the bands diminishes with increasing substitution, it appears as though the band-producing mechanism works best with the light load of the hydrogen atoms

round the ring, and is increasingly hampered by the augmentation of this load.

A similar change in intensity is observed when the spectra of ethylbenzene, styrene, and phenylacetylene are compared. An increase in the unsaturation of the side-chain produces a fall-off in the spectral luminosity.

The same rule appears to hold good in the cases of naphthalene, indene, and their reduction products. The spectra of tetrahydronaphthalene and hydrindene are much more brilliant than those of the corresponding parent substances; so it appears that an unsaturated cyclic substituent exerts a depressing influence which is at least partly removed by a saturation of the ring.

On turning to another aspect of the influence of substituents, it is found that no clear relationship can be traced between the nature of the substituents and the lengths of the spectra emitted; nor is there any regularity to be detected in the distances to which the spectra extend towards the visible region.

On the other hand, when attention is confined to substances having saturated side-chains (thus avoiding complications due to distributions of residual affinity), a rough relationship is easily traced which connects together the molecular weights of the compounds and the wave-lengths to which the spectra extend into the ultra-violet. The figures below will make the matter clear. The figure for benzene represents a very faint band which we have detected by using very low pressures of benzene vapour.

		λ.			λ.
C_6H_6	Benzene.	2544	C_9H_{10}	Hydrindene.	2702
C_7H_8	Toluene.	2602	C_9H_{12}	Mesitylene.	2703
C_8H_{10}	*m*-Xylene.	2660	$C_{10}H_{12}$	Tetrahydronaphthalene.	2719
,,	*p*-Xylene.	2673	$C_{10}H_{14}$	*p*-Cymene.	2710
,,	*o*-Xylene.	2680	$C_{18}H_{30}$	Hexaethylbenzene.	3050

Examination of this table will show that the only exceptions to the general rule—that increase in molecular weight corresponds to lessening penetration into the ultra-violet—are tetrahydronaphthalene and *p*-cymene; and in this case the difference between the two compounds is only 2 units out of a molecular weight of more than 130.

This peculiar relationship may arise from two causes. In the first place, it may represent a real connexion between the emission spectrum and the molecular weight; or, in the second place, it may be produced by an overlap between the emission and absorption spectra of the compound, so that the apparent termination of the spectrum in the ultra-violet may not be the real end of the generated spectrum but merely the point at which the emitted

spectrum can dominate the absorptive power of the compound's vapour. Evidence sufficient to decide the point is not yet available; but the behaviour of acetone proves conclusively that the Tesla-luminescence spectra do not extend indefinitely into the ultra-violet even when the absorptive power of the compound is low. Acetone emits a continuous spectrum of medium intensity which begins at wave-length 4850 and stops at 3650. This break-off in the ultra-violet cannot be due to the absorption of the acetone vapour in the cell, for it has been shown (Clarke and Stewart, *Physikal. Z.*, 1913, **14**, 1049) that even a column of *liquid* acetone 40 cm. in length only absorbs up to wave-length 3410, leaving a gap of 240 units before the luminescence spectrum begins.

With regard to the influence of position-isomerism on the spectra, the available data are limited to ethylbenzene and the xylenes. In addition to the long spectrum in the ultra-violet, *p*-xylene shows clear bands in the visible region; whilst *m*-xylene shows no more than two faint bands in the latter region. This suggests that mono-substitution or para-disubstitution is more favourable than meta-substitution for the production of this spectrum in the visible. It may be recalled that the fullest example of the visible spectrum yet obtained was observed in the case of a mono-substitution product, benzaldehyde.

The results produced by increasing unsaturation in the side-chain are seen in the cases of ethylbenzene, styrene, and phenylacetylene. The main spectrum in the ultra-violet fades more and more with increasing unsaturation. In the visible region, ethylbenzene exhibits six bands; styrene emits no banded spectrum; and phenylacetylene shows three bands. This seems to bring the case into line with the absorption spectra of these three compounds, for it has been shown that styrene has a greater absorptive power than either ethylbenzene or phenylacetylene. The influence of unsaturation in cyclic side-chains is clearly shown in the spectra of naphthalene and tetrahydronaphthalene, the former having a bright continuous band between wave-lengths 2800 and 5000, whilst the corresponding tetrahydro-derivative exhibits a very intense continuous spectrum between 2719 and 4400 and an intense band lying between 4572 and 6170. Somewhat similar results are observed in the cases of indene and hydrindene, the emission of the latter being much brighter in the visible region than the spectrum of indene.

Turning now to the effect produced by fusing a second ring to the benzene nucleus, the cases of hydrindene and tetrahydronaphthalene may be compared with that of *o*-xylene. The effect

of introducing two methyl groups into the ortho-positions in the benzene ring is two-fold. In the first place, the spectrum at the end of shorter wave-length is shifted by approximately 100 units towards the red; and, secondly, a faint spectrum makes its appearance in the visible region. Both these phenomena are traceable in the spectra of tetrahydronaphthalene and hydrindene; and it seems reasonable to ascribe them mainly to the effect of ortho-substitution upon the benzene nucleus.

Further examination shows that in the case of hydrindene, the spectrum in the visible is exceptionally brilliant, whereas the visible region of the tetrahydronaphthalene spectrum, though much brighter than the corresponding part of the *o*-xylene spectrum, is not so strong as in hydrindene. Whatever be the mechanism which produces this emission in the visible region, it is clearly more powerful in the case of the five-membered ring than in that of the six-membered ring; whilst the six-membered ring is more favourable than two separate methyl radicals.

On the other hand, when the total lengths of the three spectra are compared, it is found that the wide gap between the continuous ultra-violet spectrum and the spectrum in the visible region is diminished as we pass from *o*-xylene to hydrindene; and in the tetrahydronaphthalene spectrum the hiatus is even more markedly decreased.

The foregoing evidence establishes clearly that the Tesla-luminescence spectra are constitutional properties which are influenced even by quite minor changes in the structures of the molecules which give rise to them. In spite of this sensitiveness, however, it is possible to detect with ease certain broad general resemblances between compounds belonging to the same chemical family; and, as will be mentioned in a later paper, the Tesla-luminescence spectra can even in some cases serve as criteria of the purity of compounds and establish the identity of the material contaminating them.

We desire to acknowledge our indebtedness to the Research Fund of the Society, out of which a grant was made towards the expenses of this research.

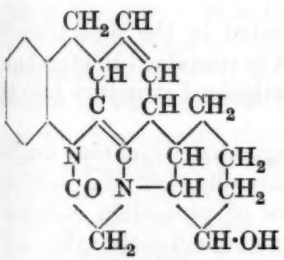
THE SIR DONALD CURRIE LABORATORIES,
THE QUEEN'S UNIVERSITY OF BELFAST,
NORTHERN IRELAND. [*Received, June 11th,* 1924.]

CCXXVII.—*Strychnine and Brucine. Part II.*

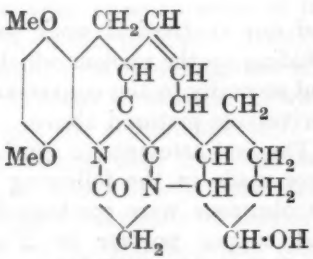
By GEORGE ROGER CLEMO, WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

ALTHOUGH, during the last fifteen years, much systematic and valuable work has been done on both strychnine and brucine by Julius Tafel, Hermann Leuchs, and others, it cannot be said that anything of real importance is known as to the structure of these alkaloids.

In a communication on "Strychnine, Berberine, and Allied Alkaloids," published in 1910 (J., **97**, 305), Perkin and Robinson gave a sketch of the state of the knowledge of the alkaloids strychnine and brucine available at that date. An attempt was made, for the first time, to deduce from the evidence which then existed, constitutional formulæ for strychnine and brucine and a detailed argument was set out in support of the view that the formulæ submitted did, in fact, account for all the properties and reactions of these alkaloids which were known at that time. The suggested formulæ were the following:



Strychnine.

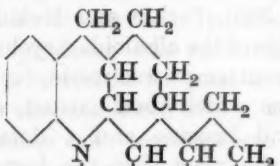


Brucine.

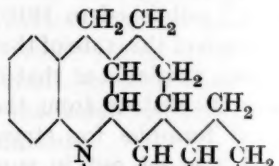
The real difficulty in forming any tangible image of the skeleton formula from which these alkaloids must be derived arises mainly from the fact that it has, so far, not been found possible, by oxidation or other means, to break up these alkaloids into sections which can be identified with substances of known constitution. Experiments with this object in view are in progress and the results of these analytical operations will, it is hoped, form the subject of a future communication. During the last few years, we have been engaged in a series of experiments having for their object the attempt to synthesise substances which, it was thought, might prove to be identical with known derivatives of strychnine or, if not identical, the examination of which might throw indirect light on the nature of the alkaloid.

Careful consideration of the whole problem suggested that the greatest chance of success was probably to be found in attempts to synthesise two of the reduction products of strychnine which had already been prepared and carefully investigated by Tafel. These are *deoxystrychnine*, formed when strychnine is reduced by hydriodic acid and phosphorus (*Annalen*, 1892, **268**, 235, 245), and *dihydrostrychnoline*, which is obtained from deoxystrychnine by further reduction first with sodium and amyl alcohol to strychnoline and then electrolytically.

The formulæ which had been suggested for these substances (*loc. cit.*, p. 311) are



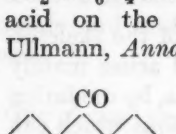
Deoxystrychnine.



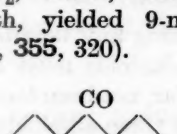
Dihydrostrychnoline.

and our synthetical work has been directed in the first place to building up the nucleus which we suggest is contained in strychnine and secondly to the conversion of the synthesised structure into the derivatives pictured above.

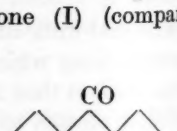
The first attempts to synthesise the suggested strychnine nucleus were made in the following way. Anthranilic acid and *o*-chloronitrobenzene were condensed in presence of potassium carbonate and copper powder to 2′-nitrodiphenylamine-6-carboxylic acid, $CO_2H{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$, which, when heated with sulphuric acid on the steam-bath, yielded 9-nitroacridone (I) (compare Ullmann, *Annalen*, 1907, **355**, 320).



(I.)



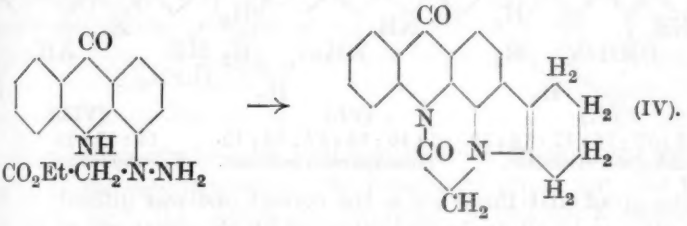
(II.)



(III.)

This nitro-derivative was reduced by ammonium sulphide to the corresponding amino-derivative and from this, by the action of bromoacetic ester, *acridone-9-aminoacetic ester* (II) was obtained, which readily yielded the *nitroso*-derivative (III).

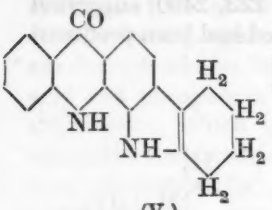
The latter substance condensed readily when its solution in acetic acid was reduced by zinc dust in presence of *cyclo*hexanone, and analogy (compare Perkin and Riley, J., 1923, **123**, 2400) suggested that the yellow, crystalline substance so obtained had been produced according to the scheme :



in which case the substance (IV) would contain the skeleton which we had attributed to strychnine. This condensation product is a weak base yielding bright yellow salts which are dissociated by water, but the *hydrochloride*, *hydrobromide*, and *nitrate* are sufficiently stable to give trustworthy results on analysis and these data, coupled with those obtained by the analysis of the base itself, leave no doubt that the formula of the base is $C_{19}H_{16}ON_2$ and not $C_{21}H_{16}O_2N_2$ (IV). It is therefore clear that at some stage of the process of reduction and condensation the acetic residue, $-CO\cdot CH_2-$, of the 9-aminoacetic ester grouping must have been removed and replaced by two atoms of hydrogen. In order to discover at what stage this unexpected elimination occurs, the nitroso-derivative of acridone-9-aminoacetic ester (III) was reduced with zinc dust and acetic acid under exactly the same conditions except that *cyclo*hexanone was not added. The result was a good yield of acridone-9-aminoacetic ester, formed no doubt by the nitroso-group being first reduced to the amino-group and then replaced by hydrogen. Clearly, then, the removal of the group $-CO\cdot CH_2-$ and its replacement by hydrogen must take place *after* or *during* the condensation with *cyclo*hexanone. The condensation product, $C_{19}H_{16}ON_2$, was carefully examined and it was found that, when its solution in alcoholic potassium hydroxide is reduced by sodium amalgam, in presence of sodium bicarbonate and carbon dioxide (a process of reduction used during this investigation in many cases with marked success; compare p. 1772), it yields a base, $C_{19}H_{18}N_2$ (m. p. 187—205°. VI) which, on oxidation, readily loses two atoms of hydrogen with the formation of a base, $C_{19}H_{16}N_2$ (m. p. 231°. VII).

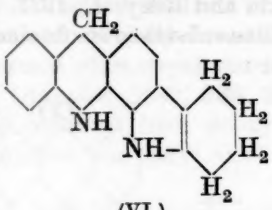
The careful consideration of the properties and compositions of these substances has led us to the conclusion that their

structural formulæ are most probably those represented by the schemes *



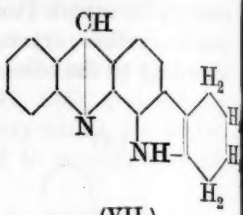
(V.)

5-*Keto*-5 : 10 : 16 : 17 : 18 : 19-*Hexahydroacrindoline.*



(VI.)

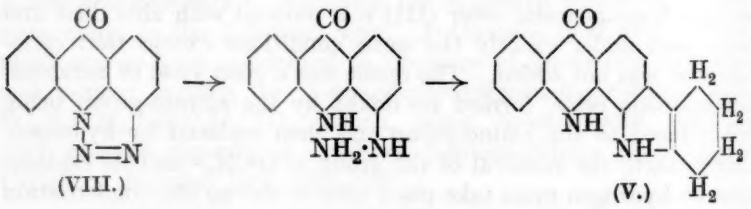
5 : 10 : 16 : 17 : 18 : 19-*Hexahydroacrindoline.*



(VII.)

16 : 17 : 18 : 19-*Tetrahydroacrindoline.*

The proof that this view is the correct one was difficult to find, but ultimately all doubt was removed by the synthesis of the base (V) by the following series of reactions. 9-Aminoacridone was converted by the action of nitrous acid into *acridonediazole* (VIII), and when this substance was reduced with zinc dust and acetic acid in presence of *cyclo*hexanone it yielded a yellow substance which, on careful comparison, was found to be identical with the condensation product (V) obtained from the nitroso-derivative of acridone-9-aminoacetic ester under the same conditions. The synthesis of this substance from acridonediazole is evidently due to the formation, in the first place, of acridone-9-hydrazine, which immediately condenses with the *cyclo*hexanone, and the resulting hydrazone, in contact with hot glacial acetic acid, then undergoes condensation in the normal manner:

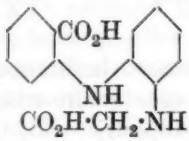


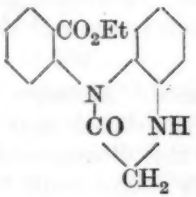
(VIII.) (V.)

As the failure of the experiments just described to bring about a synthesis of the skeleton we had suggested for strychnine was due to the unexpected loss of the $-CO\cdot CH_2-$ group and the consequent impossibility of closing the double nitrogen ring, we decided, in the next series of experiments, to ensure the closure of this ring before attempting condensation with *cyclo*hexanone. The starting point selected was 2′-aminodiphenylamine-6-carboxylic acid which we obtained from the corresponding nitro-acid by reduction with ferrous sulphate and ammonia.

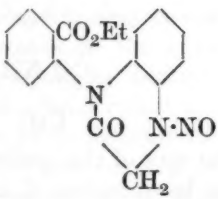
* The system of nomenclature employed in this communication is explained on p. 1769.

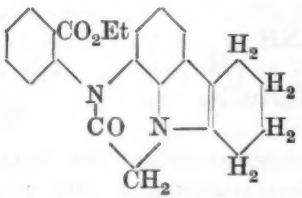
When this acid is digested with formaldehyde–sodium bisulphite, then with potassium cyanide, and finally with sodium hydroxide, it yields 6-*carboxydiphenylamine*-2′-*aminoacetic acid* (IX).

(IX.) 

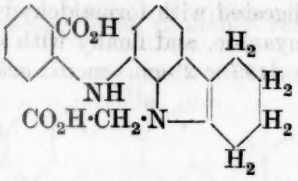
 (X.)

The action of alcoholic hydrogen chloride on this acid leads not only to the esterification of the 6-carboxyl group but also to ring closure and the substance produced is *anhydro*-6-*carbethoxydiphenylamine*-2′-*aminoacetic acid* (m. p. 153°. X). This ester yields a characteristic *nitroso*-derivative (XI), and when this substance is reduced by zinc dust and acetic acid in presence of *cyclo*hexanone, condensation takes place readily with formation of *anhydro*-8-o-*carbethoxyphenylamino*-1 : 2 : 3 : 4-*tetrahydrocarbazole*-9-*acetic acid* (m. p. 172°. XII).

(XI.) 

 (XII.)

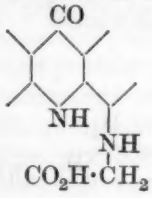
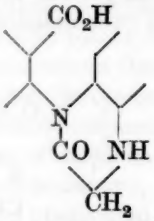
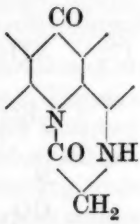
Since, in this condensation product, the lower ring is already closed, it was now only necessary to close the upper ring in order to achieve a synthesis of the supposed strychnine skeleton. In view of the fact that 2′-nitrodiphenylamine-6-carboxylic acid so readily yields nitroacridone on treatment with sulphuric acid (p. 1752), we did not anticipate that there would be any difficulty in bringing about closure of the acridone ring in the present case. Unfortunately, however, all attempts to close the acridone ring by treating the ester (XII) with sulphuric acid, phosphoryl chloride, thionyl chloride, or other dehydrating agents were quite unsuccessful; thus, for example, when sulphuric acid was employed, the ester was merely hydrolysed to the corresponding acid. The stability of the lower ring in the ester (XII) was tested by boiling with methyl alcoholic potassium hydroxide, when it was found that this treatment brings about, not only hydrolysis of the ester grouping, but also the opening of the lower ring and 8-o-*carboxyphenylamino*-1 : 2 : 3 : 4-*tetrahydrocarbazole*-9-*acetic acid* (m. p. 243°)



is produced. Attempts to close both rings simultaneously by treating this dibasic acid with dehydrating agents were unsuccessful.

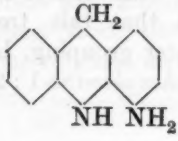
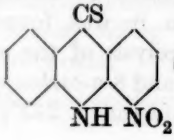
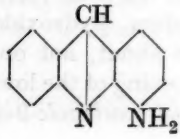
When this dibasic acid is treated with sulphuric acid, the lower ring only closes with the formation of anhydrocarboxyphenylaminotetrahydrocarbazoleacetic acid (m. p. 255°, p. 1784).

The results of the two series of experiments which have just been described clearly point to the fact that, whilst there is little difficulty in producing either of the closed ring structures (A) and (B) from the corresponding carboxylic acids by elimination of water, there is, for some reason difficult to understand, a marked disinclination to produce the double ring system (C).

(A.)  (B.)  (C.) 

It occurred to us that this obstacle in the way of the synthesis of the nucleus attributed to strychnine might be overcome if, instead of attempting to construct derivatives of acridone, in which the >CO group apparently exerts a prejudicial influence on subsequent ring closure, we replaced this group by $>CH_2$ and concentrated our attention on the synthesis of derivatives of dihydroacridine. In order to do this, it was necessary in the first place to work out the conditions for the formation of *9-amino-5 : 10-dihydroacridine* (XIII) and this substance was first obtained from 9-nitroacridone by conversion into *9-nitrothioacridone* (XIV) by the action of phosphorus pentasulphide followed by reduction with sodium amalgam.

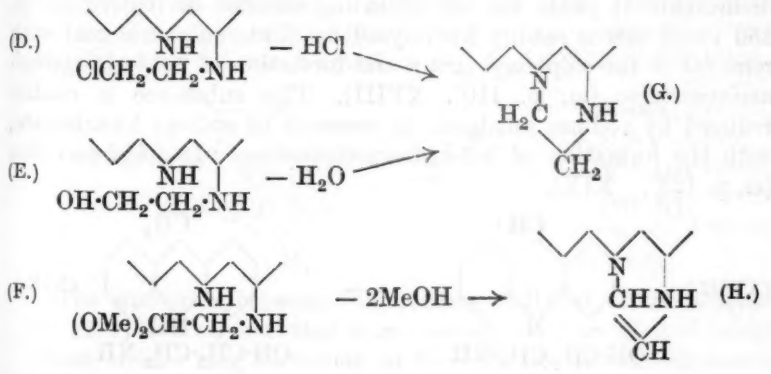
Subsequently it was found that 9-nitroacridone may be directly converted into 9-amino-5 : 10-dihydroacridine by reduction with sodium amalgam provided that special precautions are taken to prevent free alkali accumulating.

(XIII.)  (XIV.)  (XV.) 

9-*Amino*-5 : 10-*dihydroacridine* is a *colourless* crystalline substance, melts at 114°, and yields, on treatment with acetic anhydride, the *acetyl* derivative (m. p. 177°) which, on oxidation with potassium dichromate, is converted into 9-*acetylaminoacridine*. 9-*Aminoacridine* (XV), obtained by the hydrolysis of this acetyl derivative, crystallises in deep *yellow* needles and melts at 106°.

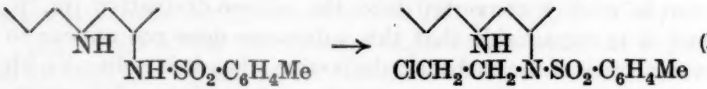
9-Aminoacridine condenses readily with chloroacetic ester with the formation of the *ester* of *acridine*-9-*aminoacetic acid* (m. p. 109°). The free acid, $C_{13}H_8N{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$ (XVI), obtained from the ester by hydrolysis, crystallises in red prisms and melts at 185°. The ester is readily converted into the *nitroso*-derivative (m. p. 117°) and it is remarkable that this substance does not appear to yield even a trace of the carbazole derivative when it is reduced with zinc dust and acetic acid in presence of *cyclo*hexanone. This unexpected and unfortunate behaviour, not observed in the case of any other similarly constituted nitroso-derivative described in this communication, is apparently due to the nitroso-group being eliminated on reduction without even the transient formation of the hydrazine.

The failure of this condensation made it evident that acridine-9-aminoacetic acid could be of no service in connexion with our experiments on the synthesis of the supposed strychnine nucleus and therefore we decided to concentrate our attention on 9-amino-5 : 10-dihydroacridine and to prepare and study systematically a number of its derivatives. Formulated as concisely as possible, the intention was to prepare substances which it was thought might subsequently yield ethano- or etheno-structures the nitroso-derivatives of which, on reduction, might condense with *cyclo*hexanone to yield substances containing the supposed strychnine nucleus. The scheme undertaken with this object in view may be pictured in partial formulæ, thus :



In order to prepare substances of these types, 9-amino-5 : 10-dihydroacridine was first combined with toluene-*p*-sulphonyl chloride and thus converted into the toluene-*p*-sulphonyl derivative (see below), which, being soluble in alkali and containing a hydrogen atom replaceable by sodium, lends itself admirably to substitution on the 9-amino-nitrogen atom.

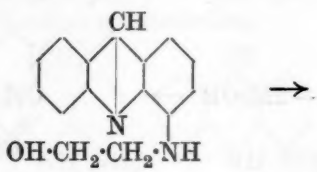
Thus, the toluene-*p*-sulphonyl derivative reacts readily with β-chloroethyl toluene-*p*-sulphonate, $C_6H_4Me{\cdot}SO_3{\cdot}CH_2{\cdot}CH_2Cl$ (J., 1922, **121**, 642), to yield the β-*chloroethyl* derivative of *toluene-p-sulphonylamidodihydroacridine* (m. p. 148°. XVII):



(XVII.)

This substance exhibits no tendency to ring closure when it is acted on by the reagents usually employed for removing hydrogen chloride.

Attention was then directed to the corresponding β-*hydroxyethyl* derivative (m. p. 155°), which is readily obtained when the potassium derivative of the toluene-*p*-sulphonyl derivative of aminodihydroacridine is digested with ethylene chlorohydrin. A series of experiments made with the object of removing water from this substance and thus closing the ring, employing, for example, phosphoryl chloride or boiling dilute sulphuric acid, led to no useful result. As it appeared possible that the lack of success in these two cases might be due to the influence of the heavy toluene-*p*-sulphonyl group in tending to remove the β-chloro- or β-hydroxy-ethyl group from proximity to the >NH group of the dihydroacridine nucleus, and thus preventing condensation, we instituted a number of experiments with the view of removing this group and succeeded by the following indirect process. When the toluene-*p*-sulphonyl derivative of 9-β-hydroxyethylaminodihydroacridine is oxidised with potassium dichromate, it yields the corresponding acridine derivative (m. p. 156°) and this is readily hydrolysed by dilute sulphuric acid with removal of the sulphonyl group and formation of 9-β-*hydroxyethylaminoacridine* (m. p. 110°. XVIII). This substance is readily reduced by sodium amalgam, in presence of sodium bicarbonate, with the formation of 9-β-*hydroxyethylamino-5 : 10-dihydroacridine* (m. p. 123°. XIX).

(XVIII.)


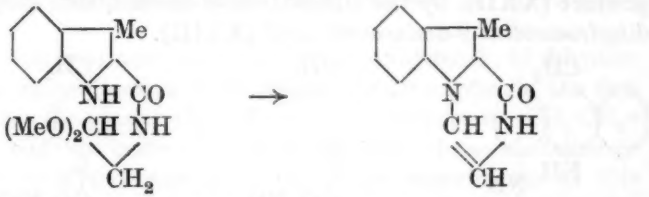
(XIX.)

A long series of experiments, described on p. 1793, was carried out in the hope that it might prove possible to induce ring closure in this substance, but without success. Thus, for example, there was no evidence of the formation of the ethano-derivative (G, p. 1757) when β-hydroxyethylaminodihydroacridine was digested with phosphoryl chloride under various conditions. This failure to induce ring formation is difficult to understand, because tetrahydrostrychnine, which in all probability contains the same grouping (E, p. 1757) that is present in β-hydroxyethylaminodihydroacridine, is converted quantitatively into strychnidine containing the grouping (G) by boiling with phosphoryl chloride.

When β-hydroxyethylaminodihydroacridine is digested with acetic anhydride, it is converted into the *diacetyl* derivative, and boiling with alcoholic hydrogen chloride for 24 hours merely removes one of the acetyl groups without any indication of ring closure. Both acetyl groups are removed when the diacetyl derivative is digested with methyl-alcoholic potassium hydroxide. Tetrahydrostrychnine exhibits a very similar behaviour since, when heated with acetic anhydride and sodium acetate, it yields a diacetyl derivative (Leuchs, *Ber.*, 1914, **47**, 538) which, on hydrolysis, loses first one acetyl group and then the other, with ultimate regeneration of tetrahydrostrychnine.

Another case of a β-hydroxyethyl derivative exhibiting the same behaviour as β-hydroxyethylaminodihydroacridine on treatment with dehydrating agents and towards acetic anhydride is that of 21-β-hydroxyethylhexahydroacrindoline (p. 1764).

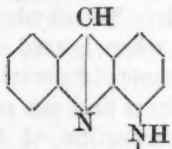
The third of this series of experiments (F, p. 1757) owed its origin to the experience, which had been gained during the researches on harmine and harmaline (J., 1921, **119**, 1613; 1922, **121**, 1874), that indolediazines are very readily formed when certain carboxyacetalylamides are treated with alcoholic hydrochloric acid, sometimes even in the cold. Thus, for example, 3-methylindole-2-carboxydimethylacetalylamide is, under these conditions, immediately converted into 5-keto-7-methyl-4 : 5-dihydroindolediazine.

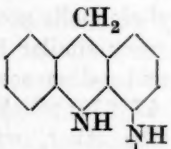


The similarity between this process and that of the scheme F (p. 1757) is so obvious that there seemed every prospect of bringing about similar ring formation in the case of the dimethylacetalyl

derivative of aminodihydroacridine and therefore we have carefully investigated this possibility. The toluene-*p*-sulphonyl derivative of 9-amino-5 : 10-dihydroacridine reacts readily with bromodimethylacetal, but the dimethylacetalylamino-condensation product (m. p. 121°) is converted into a tar when it is treated with alcoholic hydrochloric acid or sulphuric acid or acetic acid. It was then observed that bromodimethylacetal interacted with aminodihydroacridine itself in presence of sodium acetate, yielding a gum which was obviously a mixture and from which nothing crystalline could be obtained directly.

When, however, the methyl alcoholic solution of this gum was left exposed to the air, there was gradual oxidation and crystals of 9-*dimethylacetalylaminoacridine* (m. p. 87°. XX) slowly separated. This substance may be readily converted into dimethylacetalylaminodihydroacridine (m. p. 64°. XXI) by reduction with sodium amalgam in presence of sodium bicarbonate.

(XX.) 

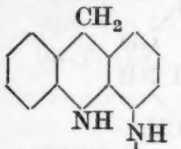


(XXI.)

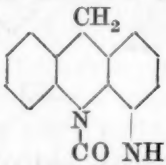
Considerable quantities of the dihydro-derivative were prepared and its behaviour with alcoholic hydrochloric acid, hydriodic acid, and with other acids, such as formic acid, acetic acid, and pyruvic acid, was investigated under a variety of conditions, but in no case was there any indication of the formation of an etheno-derivative corresponding with a dihydroindolediazine.

Anhydro-5 : 10-*dihydroacridine*-9-*aminoacetic Acid*.

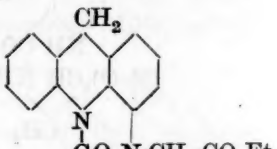
In view of the negative results which have been described in the preceding pages, there remained one possibility of synthesising the supposed strychnine nucleus and that was by combining aminodihydroacridine with bromoacetic ester and then converting the product (XXII), by the elimination of alcohol, into *anhydro*-5 : 10-*dihydroacridine*-9-*aminoacetic acid* (XXIII).



(XXII.)



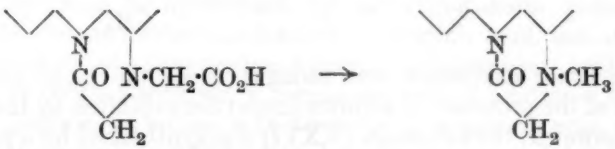
(XXIII.)



(XXIV.)

There was every reason to suppose that this substance might prove to be a valuable starting-point in our synthetical work. When the experiment was tried, we were surprised to find that the product of the action of bromoacetic ester on 9-amino-5 : 10-dihydroacridine, even without subsequent treatment with alcoholic hydrochloric acid, consisted of two substances, namely *anhydro*-5 : 10-*dihydroacridine*-9-*aminoacetic acid* (m. p. 168°, XXIII) and the *ester* of *anhydro*-5 : 10-*dihydroacridine*-9-*aminodiacetic acid* (m. p. 156°, XXIV). It was then found that the substance (XXIV) may be readily obtained from (XXIII) by the action of bromoacetic ester.

This ester (XXIV) is hydrolysed, on boiling with methyl-alcoholic potassium hydroxide, with the formation of a gum which is doubtless the dibasic acid and, on standing in methyl alcohol, the solution gradually deposits crystals of a substance, $C_{18}H_{18}O_4N_2$, which, on heating at 100°, loses methyl alcohol with the production of *anhydro*-5 : 10-*dihydroacridine*-9-*aminodiacetic acid* (m. p. 192°). Whether the methyl alcohol so removed is solvent of crystallisation or whether the substance $C_{18}H_{18}O_4N_2$ is the monomethyl ester of the dibasic acid, which seems more likely, has not been determined. In either event, the ease with which the anhydro-ring is closed is remarkable, especially in view of the lack of success experienced in attempting to close this ring in so many other cases. Anhydrodihydroacridine-aminodiacetic acid is decomposed, when strongly heated, with elimination of carbon dioxide and formation of *anhydro*-5 : 10-*dihydroacridine*-9-*methylaminoacetic acid* (m. p. 132°).



It was subsequently discovered that the substance (XXIII) may be obtained free from admixture with (XXIV) by treating amino-dihydroacridine with chloroacetic ester instead of bromoacetic ester.

Our attention was now concentrated on anhydro-5 : 10-dihydroacridine-9-aminoacetic acid (XXIII) and we attempted in the first place to reduce the group $-CO\cdot CH_2-$ in this substance to $-CH_2\cdot CH_2-$ or to $-CH{=}CH-$, in order to obtain either dihydroacridoxaline or acridoxaline itself (compare p. 1769). The experiments in this direction were unsuccessful, since the ordinary reducing agents did not yield any definite result and it was found that the substance distils unchanged from zinc dust. The action of phosphorus

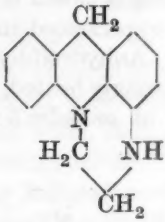
pentachloride gave rise to a complex substance containing phosphorus and chlorine which is described on p. 1789.

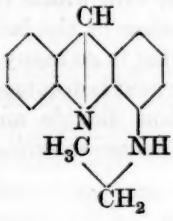
Electrolytic Reduction.—When anhydrodihydroacridineaminoacetic acid, dissolved in dilute sulphuric acid, is reduced electrolytically, it yields a sparingly soluble, crystalline sulphate, and the base obtained from this is a gum (A). This gum has a most irritating action on the skin and the solution in sulphuric acid exhibits an intense green fluorescence, properties which suggest that the base is an acridine derivative. The base yields a well-characterised acetyl derivative, $C_{15}H_{13}N_2(CO{\cdot}CH_3)$ (m. p. 152°), from which on hydrolysis it is again obtained as a gum. After distillation under reduced pressure, the base (A) gives on analysis numbers agreeing approximately with the formula $C_{15}H_{14}N_2$, and the distilled base is converted into the acetyl derivative (m. p. 152°) on boiling with acetic anhydride.

An interesting property of the base is that its solution in sulphuric acid is coloured intensely purple by potassium dichromate, a reaction reminiscent of that exhibited by strychnine itself.

Since base (A) is produced by the reduction of anhydrodihydroacridine-9-aminoacetic acid (XXIII), the most probable constitutional formula for the base would appear to be one of the following,

(XXV.)





(XXVI.)

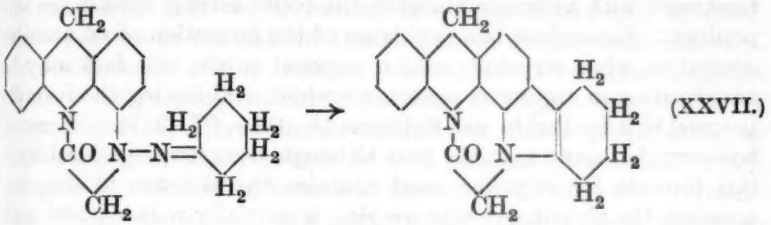
and the latter expression was thought to be the more probable because of the pronounced acridine properties exhibited by the base. When, however, the substance (XXVI) was synthesised by a method which left no doubt as to its constitution (compare p. 1787), it was found to melt at 65° and to yield an acetyl derivative melting at 95°.

It is clear, then, that the base (A) cannot have the constitution represented by (XXVI) and therefore there is every probability that it is 11 : 12-*dihydroacridoxaline* (XXV).

Synthesis of Anhydro-5 : 10 : 16 : 17 : 18 : 19-*hexahydroacrindoline*-21-*acetic Acid* (XXVII. Compare p. 1796).

Anhydro-5 : 10-dihydroacridine-9-aminoacetic acid readily yields a *nitroso*-derivative (m. p. 167°) and when this substance is reduced by zinc dust and acetic acid to the hydrazine in presence of *cyclo*-

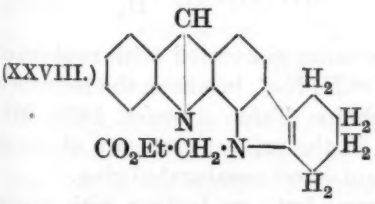
hexanone,* condensation readily occurs and *anhydrohexahydroacrindolineacetic acid*, $C_{21}H_{18}ON_2$, is obtained (XXVII):



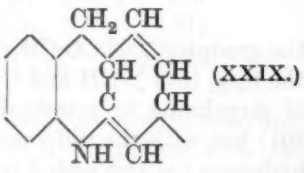
(XXVII.)

Reference to the suggested formula for strychnine (p. 1751) will show that the substance $C_{21}H_{18}ON_2$ has the same skeleton formula as strychnine, $C_{21}H_{22}O_2N_2$, and differs from it empirically in containing one oxygen atom and four hydrogen atoms less. It melts at 206°, whereas strychnine melts at 284°, and it is less basic than strychnine. It resembles strychnine in that it gives an intense purple coloration when potassium dichromate is added to its solution in acetic acid and sulphuric acid. When it is digested with methyl-alcoholic potassium hydroxide, it is hydrolysed with the formation of the corresponding *hexahydroacrindolineacetic acid*, $C_{21}H_{20}O_2N_2$, and boiling with hydrochloric acid converts this acid again into the anhydro-derivative.

This behaviour is similar to the conversion of strychnine into strychnic acid, $C_{21}H_{24}O_3N_2$, and the regeneration of strychnine by heating this acid with mineral acids. There is, however, one striking difference between the two cases which is worthy of note. When strychnine is hydrolysed by methyl-alcoholic potassium hydroxide, the only substance formed is strychnic acid, but, during the hydrolysis of anhydrohexahydroacrindolineacetic acid and subsequent contact with air, a certain amount of oxidation occurs and the product, on boiling with alcoholic hydrochloric acid, yields not only the anhydro-acid (XXVII) but also the *ester* of *tetrahydroacrindoline*-21-*acetic acid* (m. p. 172°. XXVIII).



(XXVIII.)



(XXIX.)

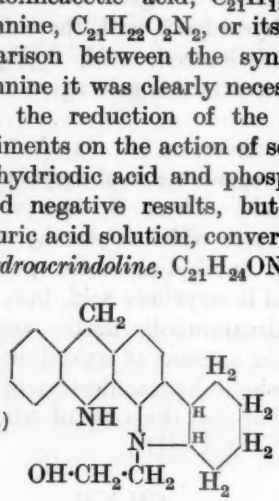
* We are also engaged in an attempt to substitute α-hydroxy*cyclo*hexanone for *cyclo*hexanone in this condensation, as this, if successful, should lead to the introduction of a hydroxyl group in the position assigned to it in the strychnine formula on p. 1751.

Indeed, if the alcoholic solution of the product of hydrolysis is allowed to stand in contact with the air for some hours before the treatment with hydrogen chloride, the above ester is almost the sole product. Since there is no evidence of the formation of an acridine derivative when strychnic acid is exposed to air, this fact may be advanced as an argument against strychnic acid having the formula assigned to it by Perkin and Robinson (J., 1910, **97**, 317). It must, however, be borne in mind that although the grouping (XXIX) in this formula for strychnic acid contains the skeleton of dihydroacridine, the right-hand benzene ring is partially reduced and such a complex may conceivably not undergo oxidation at the central grouping with the same ease as the unreduced dihydroacridine derivative certainly does.

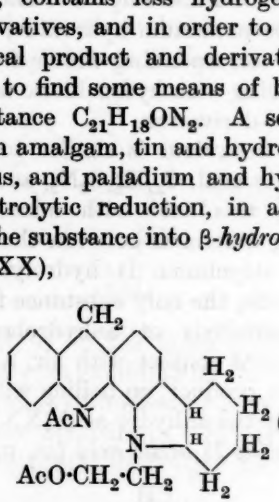
21-β-*Hydroxyethyl*-5 : 10 : 15 : 16 : 17 : 18 : 19 : 20-*octahydroacrindoline* (XXX).

It is pointed out in the last section that anhydrohexahydroacrindolineacetic acid, $C_{21}H_{18}ON_2$, contains less hydrogen than strychnine, $C_{21}H_{22}O_2N_2$, or its derivatives, and in order to make a comparison between the synthetical product and derivatives of strychnine it was clearly necessary to find some means of bringing about the reduction of the substance $C_{21}H_{18}ON_2$. A series of experiments on the action of sodium amalgam, tin and hydrochloric acid, hydriodic acid and phosphorus, and palladium and hydrogen yielded negative results, but electrolytic reduction, in alcoholic sulphuric acid solution, converted the substance into β-*hydroxyethyloctahydroacrindoline*, $C_{21}H_{24}ON_2$ (XXX),

(XXX.)



(XXXI.)



the grouping >N·CO·CH_2·N< becoming converted, with rupture of the ring, into >NH and CH_2(OH)·CH_2·N<, just as in the reduction of strychnine to tetrahydrostrychnine (Tafel, *Annalen*, 1898, **301**, 301) but with the difference that, in the present case, two atoms of hydrogen are also added to the right-hand unsaturated ring.

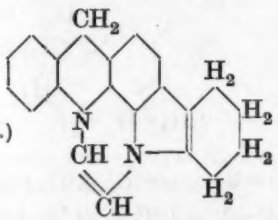
The substance (XXX) is a gum, but, on boiling with acetic anhydride, it behaves like tetrahydrostrychnine and yields a crystalline diacetyl derivative (m. p. 235°. XXXI), which dissolves in sulphuric acid to a colourless solution without fluorescence.

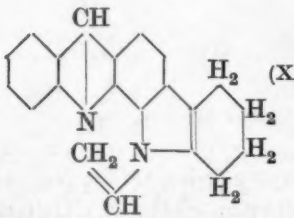
When the diacetyl derivative is hydrolysed by methyl-alcoholic potassium hydroxide, it yields a buff precipitate which now dissolves in sulphuric acid to a yellow, intensely fluorescent solution. Obviously, as in the case of the hydrolysis of anhydrohexahydroacrindolineacetic acid (p. 1763), oxidation occurs with the formation of the corresponding acridine derivative, and again this peculiarity is not shown by tetrahydrostrychnine. A characteristic of tetrahydrostrychnine is its behaviour with phosphoryl chloride, which converts it, with loss of water and closure of the ring, into strychnidine (Tafel, *loc. cit.*, p. 323), but we have so far been unable to achieve a similar change when crude β-hydroxyethyloctahydroacrindoline was treated with this reagent or when the diacetyl derivative was digested with alcoholic hydrochloric acid.

10 : 21-*Etheno*-5 : 10 : 16 : 17 : 18 : 19-*hexahydroacrindoline* (XXXII) *and its Reduction Products.*

Anhydrohexahydroacrindoline-21-acetic acid (XXVII) is partly reduced to this etheno-derivative when it is mixed with zinc dust and distilled under reduced pressure (p. 1799); on boiling the distillate with methyl-alcoholic potassium hydroxide, the unchanged material is converted into tetrahydroacrindoline-21-acetic acid (p. 1763), whereas the etheno-derivative remains unattacked. *Ethenohexahydroacrindoline*, $C_{21}H_{18}N_2$, crystallises in bright yellow needles, melts at 182° and is characterised by the striking green fluorescence of its solutions in benzene and other solvents; it has strongly basic properties and its sparingly soluble salts are bright red. With regard to the constitution of this product of the reduction of anhydrohexahydroacrindoline-21-acetic acid, two formulæ require to be carefully considered and these are the following :

(XXXII.)





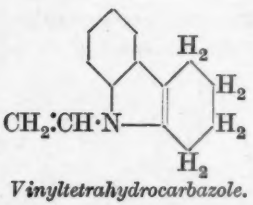
(XXXIII.)

Although it seems improbable that the anhydro-ring in anhydrohexahydroacrindolineacetic acid would suffer disruption with the formation of an acridine derivative during the course of a zinc-dust distillation, the formula (XXXIII) has been seriously discussed mainly because it accounts in a simple manner for the formation of the higher reduction derivatives (XXXV to XXXVIII), which will be dealt with immediately.

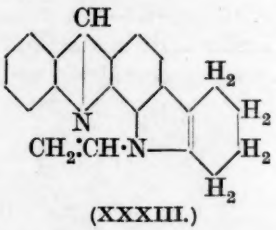
During the formation of these substances there can be little doubt that the grouping $>N\cdot CO\cdot CH_2\cdot N<$, present in the anhydro-acid, must have undergone disruption to yield $>NH$ and $CH_3\cdot CH_2\cdot N<$, and this behaviour would be at once intelligible if it is assumed that the initial disruption had occurred during the formation of the substance of m. p. 182°, in which case this substance would have the constitution (XXXIII). In spite of this, we were from the first disinclined to accept the *N*-vinyl constitutional formula (XXXIII), because experiment showed that the substance of melting point 182° may be boiled with dilute sulphuric or hydrochloric acid without decomposition and is recovered unchanged on the addition of alkali.

The small amount of evidence available clearly indicates that *N*-vinyl derivatives are unstable substances and suffer disruption, in contact with mineral acids, into acetaldehyde and the base from which they are derived. Thus, for example, it is known that methylvinylaniline, $C_6H_5\cdot NMe\cdot CH{:}CH_2$, breaks down, on boiling with dilute hydrochloric acid, into methylaniline and acetaldehyde. However, as the matter was of importance, further evidence of a more direct kind seemed to be desirable and a special investigation was therefore made into the behaviour of certain *N*-vinyl derivatives in contact with acid (see following paper).

We found, in every case examined, that the *N*-vinyl derivative was unstable and suffered disruption in the presence of mineral acid. In particular, we prepared 9-vinyltetrahydrocarbazole because of its close relationship to the compound (XXXIII),



Vinyltetrahydrocarbazole.



(XXXIII.)

and were able to show that this substance is very readily decomposed, on warming with dilute sulphuric acid, with elimination of the vinyl group and separation of tetrahydrocarbazole. This indirect evidence definitely rules out, in our opinion, the possibility that formula (XXXIII) can represent the constitution of the substance of melting point 182°.

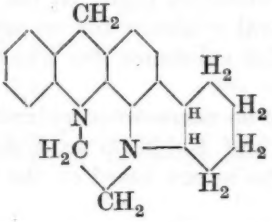
It remains to be shown that formula (XXXII) is in accord with the properties of this substance. In the first place, this formula represents the substance as a dihydroquinoxaline derivative and this is in harmony with the bright yellow colour of the crystals and

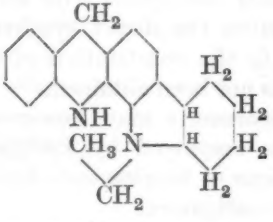
with the fact that the solutions in solvents exhibit a striking green fluorescence and that the salts are red. Otto Fischer (*Ber.*, 1891, 24, 719) has pointed out that yellow colour, brilliant green fluorescence in solution, and bright red salts are characteristics of the dihydroquinoxalines.

Dihydroquinoxalines are readily reduced to tetrahydroquinoxalines, the grouping >N·CH:CH·N< becoming converted into >N·CH_2·CH_2·N< and this behaviour is also exhibited by the substance of melting point 182°.

This substance, $C_{21}H_{18}N_2$, of melting point 182°, is readily reduced by sodium amalgam with the addition of two atoms of hydrogen to the ethylenic linking and two to the tetrahydro-ring and is converted into 10 : 21-*ethano*-5 : 10 : 15 : 16 : 17 : 18 : 19 : 20-*octahydroacrindoline*, $C_{21}H_{22}N_2$ (XXXIV), which melts at 209° and is not a derivative of dihydroacridine (as it would be if it were derived from XXXIII) because it does not yield an acetyl derivative. As in the case of the tetrahydroquinoxalines, the salts are colourless and the solutions in neutral solvents do not exhibit fluorescence.

(XXXIV.)





(XXXV.)

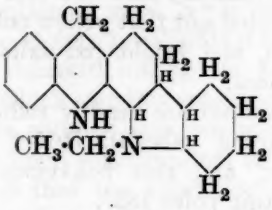
When the substance of melting point 209° is reduced electrolytically, it adds on two more atoms of hydrogen and yields a substance, $C_{21}H_{24}N_2$, which melts at 127° and is most probably 21-*ethyl*-5 : 10 : 15 : 16 : 17 : 18 : 19 : 20-*octahydroacrindoline* (XXXV).* That the grouping >N·CH_2·CH_2·N< in the substance of melting point 209° has suffered disruption during electrolytic reduction with the consequent formation of an ethyl derivative containing the dihydroacridine ring, is indicated by the fact that the substance $C_{21}H_{24}N_2$ (in contradistinction to the substance $C_{21}H_{22}N_2$) yields a characteristic acetyl derivative (m. p. 173°), from which it is regained on hydrolysis. The substance $C_{21}H_{24}N_2$ (XXXV) is not the only product of the electrolytic reduction of (XXXIV), there is also formed in considerable quantity a resinous base which distils without decomposition, has the formula $C_{21}H_{28}N_2$, and yields an acetyl derivative, $C_{21}H_{27}N_2$·CO·CH_3.

There can be little doubt that this strongly basic substance

* The ethyl group attached to nitrogen in this formula may perhaps be attached to position 10, instead of position 21, as now assumed.

is 21-*ethyl*-5 : 6 : 7 : 8 : 9 : 10 : 15 : 16 : 17 : 18 : 19 : 20-*dodecahydroacrindoline* (XXXVI),

(XXXVI.)



but we have been unable, owing to our inability to prepare crystalline derivatives and to the difficulty in obtaining any quantity of the base, to continue the examination of this interesting substance.

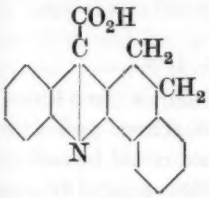
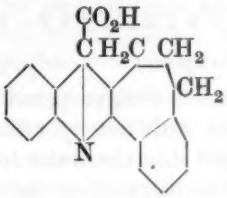
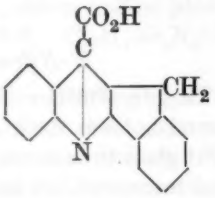
The object of this investigation has in so far been achieved that we have succeeded in preparing synthetically a number of substances which contain the complex skeleton we have associated with the structure of strychnine and brucine. On the other hand, we have not been successful in preparing a reduction product of this skeleton which would correspond with strychnoline, $C_{21}H_{26}N_2$ (m. p. 178°), and therefore the direct synthetical evidence for or against our views as to the constitution of this substance, for which we had hoped, has not been obtained.

The opportunity may, however, be taken to point out that the arguments employed by Perkin and Robinson in deducing the constitutions of brucine and strychnine are based on the results of several investigators.

A great part of this work we have repeated and are able to confirm, but unfortunately this is not the case in every instance. A fundamental assumption may on this account be unjustified, since there now appears to be no sufficient reason for regarding strychnine as a derivative of carbazole. Up to the present time, numerous attempts to repeat the work of Hanssen (*Ber.*, 1884, **17**, 2849; 1885, **18**, 777, 1917; 1887, **20**, 451) on the oxidation of strychnine by means of chromic acid have been unsuccessful.

With regard to the physiological action of the substances we have synthesised, we have submitted those numbered XXXII, XXXIV, XXXV, and XXXVI to Professor J. A. Gunn and Mr. M. H. MacKeith, who kindly undertook to examine them, and they report that none of these substances exhibits the action of strychnine on the nervous system when injected into frogs. Failure to exhibit this strychnine reaction cannot, of course, be taken to mean that these synthetical substances are not allied to strychnine, because it is well known that slight changes in constitution frequently produce profound differences in physiological behaviour. Thus, for

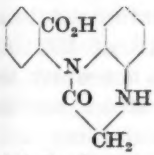
example, von Braun (*Ber.*, 1923, **56**, 1724) has recently shown that, of the following closely related substances,

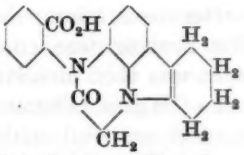
the first and second have physiological properties very similar to those of strychnine, whereas the third is inactive.

Nomenclature.

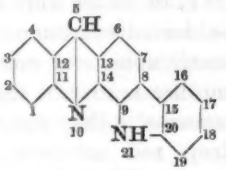
The difficult problem of providing names for the complex substances described in this communication was considered by the authors in conjunction with the Editor and it was decided to employ the following expressions and numbering.



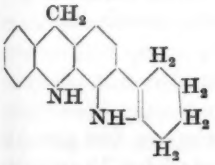
Anhydro-6-*carboxy*-*diphenylamine*-2′-*aminoacetic acid.* X.



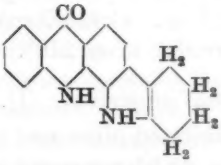
Anhydro-8-*o*-*carboxyphenyl*-*amino*-1 : 2 : 3 : 4-*tetrahydro*-*carbazole*-9-*acetic acid.* XII.



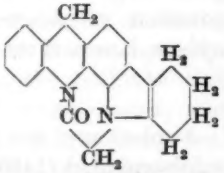
Acrindoline.



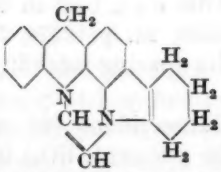
5 : 10 : 16 : 17 : 18 : 19-*Hexahydroacrindoline.* VI.



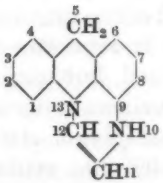
5-*Keto*-5 : 10 : 16 : 17 : 18 : 19-*hexahydroacrindoline.* V.



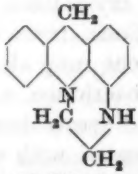
Anhydro-5 : 10 : 16 : 17 : 18 : 19-*hexahydroacrindoline*-21-*acetic acid.* XXVII.



10 : 21-*Etheno*-5 : 10 : 16 : 17 : 18 : 19-*hexahydroacrindoline.* XXXII.



Acridoxaline.



11 : 12-*Dihydroacrid*-*oxaline.* XXV.

The bridge-bond formula for acridine is employed throughout the present communication on account of the convenience attending the representation,

in this manner, of the relations of acridine with dihydroacridine and acridine derivatives, but this must not be taken to imply approval of the formula on a theoretical basis.

EXPERIMENTAL.

2'-Nitrodiphenylamine-6-carboxylic Acid.

Large quantities of this acid were prepared as follows: In a 1500 c.c. round-bottom flask fitted with a very efficient stirrer and with a bent glass tube so arranged that the water formed could be collected and measured, an intimate mixture of anthranilic acid (137 gms.), *o*-chloronitrobenzene (200 gms.), potassium carbonate (138 gms.), and copper (0·2 gm.) was heated, first at 200°, when the formation of potassium anthranilate occurred, 9 c.c. of water were collected, and the whole set to a nearly solid mass, and then at 220°, when the mass slowly changed to a rather viscid but easily stirred syrup, which became deep red owing to the formation of the potassium salt of the condensation product. During this change, a further 9 c.c. of water were slowly collected together with about 16 gms. of *o*-chloronitrobenzene and, after 1—2 hours, the mixture set to an unstirrable, red solid. The heating was continued at 220° for another hour and the product was then dissolved in hot water, the excess of *o*-chloronitrobenzene (28 gms.) distilled in steam, and the deep red solution cooled, and acidified with hydrochloric acid. The olive-green precipitate, after being well washed with hot water and dried on the steam-bath, weighed about 230 grams (yield 90 per cent.), melted at 195—205°, and was pure enough for the preparation of 9-nitroacridone. Crystallised from acetic acid or xylene, it separates in needles, m. p. 219°.

9-Nitroacridone (I).

A solution of the precipitated nitro-acid (see above; 200 gms.) in sulphuric acid (1400 gms. of 95 per cent.) is heated for 15 minutes on the steam-bath and poured on to ice. The crude nitroacridone is collected, boiled with water, then with dilute sodium carbonate, again with water, dried (weight 150 gms.; m. p. about 250—260°), and crystallised from boiling nitrobenzene (700 c.c.), best in three portions, from which it separates in needles, m. p. 257—258°. Xylene may also be used, but, owing to the sparing solubility of nitroacridone, a large volume is necessary.

9-Nitroacridone-3(?)-sulphonic Acid.—9-Nitroacridone (48 gms.) is heated with oleum (96 c.c., containing 20 per cent. SO_3) for 2 hours on the steam-bath. The product is poured on to ice, treated with excess of chalk, filtered hot, the filtrate evaporated to about 200 c.c., mixed with sodium carbonate (11 c.c.), again filtered, and evaporated, when 57 gms. remain. That this mass is the sodium

salt of a monosulphonic acid was proved by heating the dry salt (5 gms.) with phosphorus pentachloride (6 gms.) for ½ hour at 120—140° and crystallising the product from xylene, when yellow plates were obtained, m. p. 270—274° (Found : S = 9·6. $C_{13}H_{17}O_5N_2ClS$ requires S = 9·4 per cent.).

9-*Aminoacridone*.—Ullmann's method (*Annalen*, 1907, **355**, 329) of reducing the nitro-derivative with sodium sulphide does not work well, except with small quantities, and is apt to become violent. We obtained large quantities of aminoacridone by the following method. 9-Nitroacridone (50 gms.), alcohol (500 c.c. of 95 per cent.), and ammonia (150 c.c. of *d* 0·88) are gently refluxed for 5 hours while a steady stream of hydrogen sulphide is passed. After 12 hours, ammonia (50 c.c.) and alcohol (50 c.c.) are added and the refluxing and passage of hydrogen sulphide continued for five hours. The mixture is again left over-night, saturated with hydrogen sulphide, and the whole rapidly filtered, when a bright yellow solid (48 gms.) results. This is dried, extracted twice with boiling xylene, to remove sulphur, when nearly pure aminoacridone (34 gms.) remains. This substance, which does not melt at 340°, was employed for all the syntheses described in this communication. 9-Aminoacridone dissolves in concentrated sulphuric acid to a pale yellow solution which exhibits an intense blue-green fluorescence.

Acridonediazole (VIII).

9-Aminoacridone (8·2 gms.), sulphuric acid (50 c.c. of 20 per cent.), and ice are vigorously stirred and a dilute aqueous solution of sodium nitrite (3·5 gms.) gradually added. The stirring is continued for an hour, the reaction mixture brought just to the boil, the buff precipitate collected, thoroughly washed with warm water, and dried on the steam-bath. The diazole, of which a nearly theoretical yield was obtained, was nearly pure; m. p. 258—262° (decomp.). It separated from glacial acetic acid in brown prisms, m. p. 266° (decomp.) (Found : C = 70·5; H = 3·4; N = 18·6. $C_{13}H_7ON_3$ requires C = 70·6; H = 3·2; N = 19·0 per cent.).

5-*Keto*-5 : 10 : 16 : 17 : 18 : 19-*hexahydroacrindoline* (V).

Acridonediazole (5 gms.), suspended in glacial acetic acid (50 c.c.), is mixed with *cyclo*hexanone (8 c.c.), warmed to 30°, and then zinc dust (13 gms. of 90 per cent.) gradually added, the whole being vigorously shaken in a corked flask and care being taken that the temperature, which is apt to rise considerably, does not exceed 45°. After 6 minutes, the whole is cooled, filtered to remove unchanged zinc dust, and the filtrate allowed to remain over-night. The yellow precipitate, even after being thoroughly washed with dilute hydro-

chloric acid and then with ammonia, contains a trace of zinc (Found: C = 78·6; H = 5·8; N = 9·6. $C_{19}H_{16}ON_2$ requires C = 79·2; H = 5·5; N = 9·7 per cent.). If the deep brown mother-liquors from this crystallisation are heated on the steam-bath for an hour and allowed to remain over-night, a further small crop of crystals separates (total yield about 2·8 gms.). On adding sodium nitrite to the filtrate from this second crop, a considerable separation of acridonediazole takes place.

Ketohexahydroacrindoline does not melt at 380°. It is very sparingly soluble in the usual solvents; may be recrystallised from nitrobenzene, from which it separates in glistening, old-gold prisms, and dissolves readily in hot methyl-alcoholic potassium hydroxide, being reprecipitated by dilute acetic acid, but not by water alone. The solution in concentrated sulphuric acid is nearly colourless, exhibits a remarkable pale blue fluorescence, and on the addition of water becomes yellow and deposits a yellow, crystalline sulphate. The addition of nitric acid or potassium dichromate gives a reddish-brown coloration which fades on warming. The *hydrochloride*, *hydrobromide*, *nitrate*, and *sulphate* of this base are described on p. 1777.

5 : 10 : 16 : 17 : 18 : 19-*Hexahydroacrindoline* (VI).

This substance is obtained when ketohexahydroacrindoline (see the previous section) is reduced in alcoholic solution with sodium amalgam under the following special conditions. The substance (14·4 gms.), sodium hydrogen carbonate (24 gms.), and alcohol (160 c.c.) are placed in a 750 c.c. flask fitted with a stirrer, reflux condenser, inlet tube (A), dipping well under the surface of the alcohol, and a wider tube (B) closed with a cork. The flask is placed in a water-bath heated at 75°, the contents are vigorously stirred, a slow stream of carbon dioxide is passed through the inlet tube (A), and then crushed sodium amalgam (160 gms. of 4 per cent.) added through (B) during 1½ hours.

The temperature is raised to 80° and kept at this for 3 hours and during the next hour a further quantity of sodium amalgam (80 gms.) is gradually added, the temperature is then raised to 80—85°, the stirring and passage of carbon dioxide being continuous throughout the whole operation. The product is filtered hot, the residue boiled with alcohol, again filtered, and the combined filtrates are reduced to about 100 c.c. by distillation under reduced pressure and left over-night. The crystalline deposit is collected, boiled with water to remove traces of inorganic matter, and dried on the steam-bath, when the yellow mass (10—12 gms.) melts at 185—210°. This crystallises well from light petroleum (b. p. 100—120°) in

yellow plates which, in spite of the fact that the melting point is indefinite at 187—205°, are seen under the microscope to be quite homogeneous (Found : C = 82·9; H = 6·7; N = 10·1. $C_{19}H_{18}N_2$ requires C = 83·2; H = 6·6; N = 10·2 per cent.).

Hexahydroacrindoline is readily soluble in boiling benzene, but sparingly soluble in the cold and separates in microscopic groups of needles, m. p. about 187—205°. The addition of picric acid to the solution in benzene causes the picrate to separate as a reddish-brown substance like amorphous phosphorus. Hexahydroacrindoline is coloured deep red by sulphuric acid, and hydrochloric acid converts it into a bright red hydrochloride which, on boiling with water, changes to a black resin. A hydrochloride is obtained in brilliant red prisms when a boiling alcoholic solution of the base is mixed with alcoholic hydrochloric acid and allowed to stand and it is probable that this is the hydrochloride of tetrahydroacrindoline. The hexahydro-base dissolves readily in acetic acid and on dilution with water the acetate is dissociated with separation of a yellow precipitate.

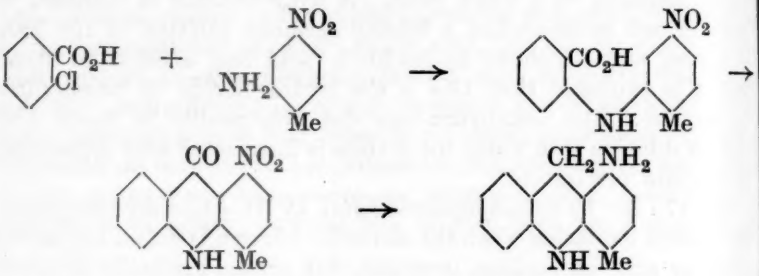
16 : 17 : 18 : 19-*Tetrahydroacrindoline* (VII).—Hexahydroacrindoline suffers oxidation when the alcoholic solution is boiled in contact with air and, on cooling, irregular, flat prisms gradually separate which, after recrystallisation from alcohol, melt at 230—231° and consist of *tetrahydroacrindoline* (Found : C = 83·3; H = 5·9; N = 10·2. $C_{19}H_{16}N_2$ requires C = 83·8; H = 5·9; N = 10·3 per cent.). This base is coloured brick-red by concentrated hydrochloric acid and the hydrochloride or the sulphate may be obtained as brilliant red, crystalline precipitates by adding hydrochloric acid or sulphuric acid to the solution of the base in glacial acetic acid. The base dissolves to a pale yellow solution in concentrated sulphuric acid which exhibits a pale yellow fluorescence and the addition of a drop of nitric acid intensifies the colour and destroys the fluorescence. Dilution with water causes the pale yellow solution in sulphuric acid to become deep orange-red and the addition of potassium dichromate produces a brown coloration.

The base is readily soluble in warm benzene, yielding a solution which has a slight green fluorescence, and on mixing with a solution of picric acid in benzene, a deep red, crystalline picrate separates. The base dissolves readily in boiling methyl alcohol and separates, on slow cooling, as a mass of deep yellow needles which when dry have the appearance of old gold. Tetrahydroacrindoline is readily converted into the hexahydro-derivative when its solution in boiling alcohol is treated with sodium amalgam and the latter substance separates on addition of water as a yellow precipitate,

which crystallises from ligroin in yellow prisms and again has the indefinite melting point 185—205°.

6-*Nitro*-9-*methylacridone and* 6-*Amino*-9-*methyl*-5 : 10-*dihydroacridine.*

6-Nitro-9-methylacridone was prepared with the object of determining whether the reactivities of the >CO and $-NO_2$ groups in this substance were similar to or different from the reactivities of the corresponding groups in 9-nitroacridone (p. 1770). It is readily obtained and converted into 6-amino-9-methyl-5 : 10-dihydroacridine according to the scheme :



A mixture of *o*-chlorobenzoic acid (15·6 gms.), 4-nitro-*o*-toluidine (15·2 gms.), potassium carbonate (7 gms.), a trace of copper powder, and anhydrous amyl alcohol (50 c.c.) was boiled for 30 hours, the alcohol removed by distillation in steam, sodium hydroxide (70 c.c. of 8 per cent.) added and, after remaining over-night, the solution, filtered from unchanged nitro-*o*-toluidine, was acidified, when crude 4-nitrotolylanthranilic acid (15 gms.) separated. This was boiled with water to remove unchanged *o*-chlorobenzoic acid and converted into 6-nitro-9-methylacridone by treatment with sulphuric acid, essentially under the conditions described in detail in the preparation of 9-nitroacridone (p. 1770). This substance separates from nitrobenzene in small, deep yellow prisms which do not melt at 300° (Found : N = 10·9. $C_{14}H_{10}O_3N$ requires N = 11·0 per cent.).

6-*Amino*-9-*methyl*-5 : 10-*dihydroacridine.*—When the nitromethylacridone just described is treated with sodium amalgam in presence of sodium hydrogen carbonate, in the apparatus and under the conditions described on p. 1772, it readily yields the corresponding *dihydroacridine*, which separates from light petroleum in long, bright orange prisms, m. p. 118° (Found : C = 80·3; H = 6·8. $C_{14}H_{14}N_2$ requires C = 80·0; H = 6·7 per cent.). This amino-derivative is much more stable than 9-amino-5 : 10-dihydroacridine (p. 1785) and may be exposed to the air, apparently indefinitely, without oxidation to the acridine occurring. It is converted into a

colourless crystalline sulphate by sulphuric acid (50 per cent.) and a reddish-brown solution is obtained on the addition of potassium dichromate. These substances have other interesting properties, and we propose to investigate them in greater detail.

9-Chloro-5 : 10-dihydroacridine and 9-Chloroacridine.

9-Chlorodihydroacridine is obtained when 9-chloroacridone (Ullmann, *Annalen*, 1907, **355**, 337) is reduced by sodium amalgam in presence of sodium hydrogen carbonate (compare p. 1772) and separates from light petroleum (b. p. 80—100°) in very pale yellow, irregular prisms, m. p. 76° (Found : C = 72·3; H = 4·9. $C_{13}H_{10}NCl$ requires C = 72·4; H = 4·6 per cent.). This substance is readily oxidised when potassium dichromate is added to the solution in glacial acetic acid and yields 9-*chloroacridine*, which separates from light petroleum in two distinct crystalline modifications. If the solution in light petroleum (b. p. 80—100°) is rapidly cooled, the labile modification separates in needles, m. p. 79°, but, on standing, these change into pale yellow, irregular prisms of the stable modification (m. p. 90—91°) (Found : C = 73·6; H = 4·0. $C_{13}H_8NCl$ requires C = 73·1; H = 3·7 per cent.). This chloroacridine was prepared with the object of converting it into 9-ethylaminoacridine, but interaction did not take place when the substance was heated with ethylamine (2 mols.) in a sealed tube at 160° for some hours. Subsequently this ethylamino-derivative was obtained from the toluene-*p*-sulphonyl derivative of 9-aminoacridone by the process described on p. 1787.

Acridone-9-aminoacetic Acid (II) *and its Derivatives.*

This acid may be prepared by heating 9-aminoacridone (p. 1771; 22 gms.), suspended in alcohol (50 c.c.), with bromoacetic ester (20 gms.) in a reflux apparatus for 2 days on the steam-bath. The viscid deep brown product is distilled in steam until all the alcohol and excess of bromoacetic ester have passed over, the solid is collected, washed well, dried, and digested with methyl-alcoholic potassium hydroxide (100 c.c. of 10 per cent.) for ½ hour. Water is added and, after 12 hours, the alkaline solution is filtered from a considerable quantity of a dark brown substance * and acidified with acetic acid, when a yellowish-brown precipitate of crude acridone-9-aminoacetic acid separates which is washed well with water, then once with alcohol, and dried on porous porcelain. This

* This precipitate is boiled with dilute ammonia, collected, dried, and extracted twice with hot alcohol; the residue is nearly pure 9-aminoacridone and can be used in a subsequent preparation.

curious gelatinous acid cannot be recrystallised and is purified by conversion into the characteristic methyl or ethyl ester.

The Methyl Ester.—The crude dry acid dissolves in methyl alcohol saturated with hydrogen chloride and a splendid crimson, crystalline precipitate of the hydrochloride of the methyl ester gradually separates. The crimson paste is washed with methyl-alcoholic hydrochloric acid and mixed with water, which does not dissociate the salt, but, on the addition of dilute ammonia, the precipitate loses its red colour and the free yellow methyl ester is obtained. This is washed well and recrystallised from methyl alcohol, in which it is sparingly soluble and from which it separates as a hard crust of deep yellow prisms, m. p. 237—238° (Found: C = 68·4; H = 5·2; N = 9·8. $C_{16}H_{14}O_3N_2$ requires C = 68·1; H = 5·0; N = 9·9 per cent.).

A trace of this methyl ester dissolves in sulphuric acid to a colourless solution which exhibits a fine pale blue fluorescence, and a crystal moistened with nitric acid is first coloured red and then dissolves to an intense sage-green solution.

The Nitroso-derivative.—The methyl ester is moderately soluble in methyl alcohol containing hydrogen chloride and, on addition of aqueous sodium nitrite to the deep red solution of the hydrochloride, the colour changes to green and soon, especially on rubbing, the nitroso-derivative begins to separate in groups of long, well-defined prisms; the mother-liquor gives a further considerable crop on dilution with water. The substance separates from dilute acetic acid in nearly colourless leaflets, shrinks at 170°, and decomposes at about 180° with evolution of gas (Found: C = 62·0; H = 4·4; N = 13·6. $C_{16}H_{13}O_4N_3$ requires C = 61·7; H = 4·2; N = 13·5 per cent.).

The Ethyl Ester.—This ester has been prepared in considerable quantities for use in the synthetical experiments described on p. 1778. Crude dry acridone-9-aminoacetic acid (25 gms.), suspended in absolute alcohol (160 c.c.), was rapidly saturated with hydrogen chloride so that the liquid almost boiled, when the acid dissolved completely to a red solution. As soon as saturation was nearly complete, the crimson hydrochloride commenced to crystallise and this then gave place to an ochre precipitate consisting apparently of the dihydrochloride. When this precipitate was collected with the aid of the pump and washed with a little alcohol, it changed again to red and, on rubbing with dilute ammonia, the pale yellow ethyl ester separated. This is much more soluble in alcohol than the methyl ester and separates from 50 per cent. alcohol as a voluminous mass of yellow needles which shrink at 190° and melt at 195° (Found: C = 69·2; H = 5·4; N = 9·5. $C_{17}H_{16}O_3N_2$ requires C = 68·9;

H = 5·4; N = 9·4 per cent.). This *ethyl* ester dissolves readily in hot alcohol, acetone, or acetic acid, but is sparingly soluble in benzene; like the methyl ester, it dissolves in sulphuric acid to a colourless solution exhibiting a striking pale blue fluorescence.

The Nitroso-derivative.—The ester (1 gm.), dissolved in the minimum of alcohol, was mixed with alcoholic hydrogen chloride (1 c.c. of 20 per cent.) and then sodium nitrite (0·6 gm.), dissolved in a little water, added, the temperature being kept at 10°. A grey powder separated and increased in quantity on addition of water. This was collected, washed well, and recrystallised from alcohol, in which it was sparingly soluble and from which it separated as a slightly brown, glistening, silky mass melting at 185—186° with vigorous effervescence to a black froth (Found: C = 63·2; H = 4·7; N = 12·9. $C_{17}H_{15}O_4N_3$ requires C = 62·8; H = 4·6; N = 12·9 per cent.).

Condensation of Ethyl Acridone-9-nitrosoaminoacetate with cyclo-*Hexanone. Formation of* 5-*Keto*-5 : 10 : 16 : 17 : 18 : 19-*hexahydroacrindoline* (V; compare pp. 1753, 1771).

When the above nitroso-derivative (5 gms.), suspended in glacial acetic acid (30 c.c.), is mixed with *cyclo*hexanone (8 c.c.) and zinc dust (15 gms. of 90 per cent.) gradually added with vigorous shaking, the nitroso-derivative rapidly passes into solution with some evolution of heat. The temperature is kept below 45° and after 4 or 5 minutes the whole is rapidly filtered from unchanged zinc, which is washed with a little glacial acetic acid.* The deep yellow-brown filtrate, on heating on the steam-bath, soon begins to deposit yellow crystals of the ketohexahydroacrindoline and, after ½ hour, the mass is collected and washed with acetic acid. The glistening, yellow, crystalline mass is ground with dilute hydrochloric acid to remove zinc, the light orange hydrochloride collected, washed thoroughly with warm dilute hydrochloric acid and finally with warm dilute ammonia, and dried in the steam-bath (Found: C = 78·6; H = 5·7; N = 9·6. $C_{19}H_{16}ON_2$ requires C = 79·2; H = 5·5; N = 9·7 per cent.). The substance dissolves readily and completely in alcoholic potassium hydroxide and, on dilution with much water, a yellow, crystalline precipitate separates. After being washed with alcohol, the substance is nearly colourless (Found: C = 78·9; H = 5·6; N = 9·6 per cent.).

The Hydrochloride, $C_{19}H_{16}ON_2$,HCl.—The powdered and finely

* If the zinc residues are digested with dilute hydrochloric acid on the steam-bath until the zinc has completely dissolved, a further quantity of less pure condensation product separates and this may be obtained pure by conversion into the hydrochloride and decomposition with ammonia.

sieved base (1 gm.) does not dissolve in boiling glacial acetic acid (20 c.c.), showing that the substance is not basic enough to yield an acetate.

When, however, concentrated hydrochloric acid (5 c.c.) is added, a clear solution is obtained which immediately begins to deposit orange crystals of the hydrochloride. This is washed with acetic acid (2 parts) and hydrochloric acid (1 part), drained on porous porcelain, and dried at 100° (Found : C = 70·1 ; H = 5·2. $C_{19}H_{16}ON_2$,HCl requires C = 70·1 ; H = 5·2 per cent.).

When this orange hydrochloride is boiled with water, it is dissociated, the colour disappears, and the base separates as an almost colourless, crystalline precipitate.

The Hydrobromide, $C_{19}H_{16}ON_2$,HBr.—When the suspension of the base (1 gm.) in boiling glacial acetic acid (20 c.c.) is mixed with concentrated hydrobromic acid, a clear solution is not formed as in the case of the hydrochloride (see above), but the red-ochre, crystalline hydrobromide separates at once. This is washed with acetic acid containing hydrobromic acid and dried at 100° (Found : C = 62·0 ; H = 4·9. $C_{19}H_{16}ON_2$,HBr requires C = 61·8 ; H = 4·6 per cent.). This salt also is dissociated by boiling water.

The Nitrate.—On the addition of nitric acid to the suspension of the base in warm acetic acid, a pale brown, fluorescent solution is produced and a gum soon separates which, on rubbing, crystallises and the solution becomes filled with yellow crystals. This salt is collected, washed with acetic acid containing nitric acid, and dried at 100° (Found : C = 65·6 ; H = 5·0 ; N = 11·6. $C_{19}H_{16}ON_2$,HNO_3 requires C = 65·0 ; H = 4·8 ; N = 12·0 per cent.).

The Sulphate.—When sulphuric acid, diluted with acetic acid, is added to the suspension of the base in warm glacial acetic acid, a clear orange fluorescent solution is produced from which deep yellow crystals (consisting of microscopic balls of yellow needles) gradually separate. Once separated, this salt is very sparingly soluble in boiling glacial acetic acid.

That the base (A) obtained by the condensation of ethyl acridone-9-nitrosoaminoacetate with *cyclo*hexanone in presence of zinc has the composition $C_{19}H_{16}ON_2$ is clearly established by the experimental investigation described above. That it is identical with the base—5-keto-5 : 10 : 16 : 17 : 18 : 19-hexahydroacrindoline (p. 1771)—obtained when acridonediazole is condensed under the same conditions with *cyclo*hexanone, was proved by direct comparison and especially by the following facts. On reduction, in alcoholic solution with sodium amalgam (compare p. 1772), the base (A) yields 5 : 10 : 16 : 17 : 18 : 19-hexahydroacrindoline (m. p. 187—205°), as is evidenced by the fact that, on oxidation in contact with air, it

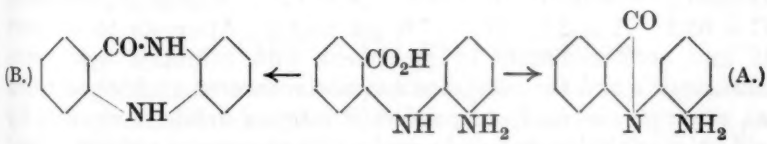
is converted into 16 : 17 : 18 : 19-tetrahydroacrindoline (m. p. 230—231°, p. 1773). In the last case, identity was demonstrated not only by analysis but also by the method of mixed melting points.

2′-Aminodiphenylamine-6-carboxylic Acid.

The mixture obtained by adding hot aqueous ferrous sulphate (625 gms. in 750 c.c.) to the nitro-acid (p. 1752) (65 gms. in ammonia, 270 c.c., and water, 270 c.c.) during 15 minutes is filtered hot and the sludge washed twice with dilute ammonia. The filtrate, treated with (*a*) sulphur dioxide, or (*b*) hydrochloric acid, gives (*a*) 45 gms. of crude *2′-aminodiphenylamine-6-carboxylic acid*, prisms from xylene, m. p. 210° (decomp.) (Found : N = 12·0. $C_{13}H_{12}O_2N_2$ requires N = 12·3 per cent.), or (*b*) its *hydrochloride*, prisms from alcohol, m. p. 260°.

Anhydro-2′-aminodiphenylamine-6-carboxylic acid (*2′-aminophenylanthranil*), yellow plates from aqueous pyridine, m. p. 250° (Found : C = 73·9; H = 5·0; N = 13·2; *M*, in camphor by Rast's method, = 217. $C_{13}H_{10}ON_2$ requires C = 74·3; H = 4·8; N = 13·3 per cent.; *M* = 210), is obtained from the preceding acid at its m. p. or in boiling xylene. It forms an *acetyl* derivative, plates from xylene, m. p. 248° (Found : C = 71·7; H = 5·0; N = 10·9. $C_{15}H_{12}O_2N_2$ requires C = 71·4; H = 4·8; N = 11·1 per cent.), when boiled with acetic anhydride and a drop of sulphuric acid for 10 minutes, and yields a colourless sulphate with 50 per cent. sulphuric acid; this mixture develops with dichromate an intense permanganate coloration which becomes deep red on addition of water.

With regard to the constitution of this anhydro-acid, there are two ways in which water may be eliminated from 2′-aminodiphenylamine-6-carboxylic acid to yield a substance $C_{13}H_{10}ON_2$,



and we incline to the view that (B) is the correct representation of the constitution of the substance, since all its properties harmonise therewith. Thus the anhydro-acid does not appear to diazotise on treatment with nitrous acid and it is readily hydrolysed to the salt of the amino-acid on boiling with methyl alcoholic potassium hydroxide. The ready formation of the anhydro-derivative by the action of heat on the amino-acid points to (B) and makes the anthranil structure (A) unlikely, because anthranil itself is not produced by the

action of heat on anthranilic acid (compare Bamberger, *Ber.*, 1903, **36**, 3648; 1906, **42**, 1647; also Heller, *Ber.*, 1904, **37**, 976). When anthranilic acid is heated, it either sublimes or decomposes into carbon dioxide and aniline.

Confirmatory evidence in favour of structure (B) is furnished by the observation that the solution of the substance in glacial acetic acid yields, on treatment with aqueous sodium nitrite, a *nitroso*-derivative. This separates from alcohol in flat, irregular, six-sided, pale brown prisms which darken on heating and melt with decomposition at 202° (Found : N = 17·4. $C_{13}H_9O_2N_3$ requires N = 17·6 per cent.). This substance dissolves in concentrated sulphuric acid to a violet solution and, on the addition of ice, a deep indigo colour results which quickly fades to brown.

Flavinduline-o-carboxylic Acid, $\begin{matrix} C_6H_4\cdot C \\ | \\ C_6H_4\cdot C\cdot NCl(C_6H_4\cdot CO_2H) \end{matrix} \!\!>\!\! N\!\!>\!\! C_6H_4.$

The hydrochloride of 2′-aminodiphenylamine-6-carboxylic acid (5·24 gms.) and phenanthraquinone (4·16 gms.) are digested together in glacial acetic acid solution for 2½ hours, concentrated hydrochloric acid (5 c.c.) is added and, after 12 hours, the brown, prismatic plates are collected and dried on the steam-bath, when 8 gms. of the dye are obtained, m. p. 310° (decomp.). The substance may be crystallised from acetic acid without alteration of melting point (Found : N = 5·93. $C_{27}H_{17}O_2N_2Cl$ requires N = 6·4 per cent.).

1-o-*Carboxyphenyl*-1 : 2 : 3-*benztriazole*, $CO_2H\cdot C_6H_4\cdot \begin{matrix} N \\ | \\ N \end{matrix} \!\!-\!\! \begin{matrix} C_6H_4 \\ | \\ =N \end{matrix}$.

This substance, prepared in a similar manner to the diazole of acridone (p. 1771), crystallised in colourless, glistening plates which melted with explosive decomposition at about 217° (Found : C = 65·0; H = 3·8; N = 17·7. $C_{13}H_9O_2N_3$ requires C = 65·3; H = 3·7; N = 17·6 per cent.). Attempts to convert it into acridonediazole by treatment with sulphuric acid were unsuccessful and the substance was also recovered unchanged when an attempt was made to convert it into an indole derivative by reduction with zinc dust and acetic acid in presence of *cyclo*hexanone.

6-*Carboxydiphenylamine*-2′-o-*aminobenzoic Acid and* s.-*Diphenyl*-o-*phenylenediamine*.

o-Phenylenediamine (2·7 gms.), *o*-chlorobenzoic acid (7·8 gms.), potassium carbonate (6·9 gms.), and a trace of copper are boiled with water (50 c.c.) for 24 hours. Aqueous sodium carbonate is added, the intense purple solution filtered hot and mixed with excess of hydrochloric acid. The blue precipitate is collected, extracted

three times with boiling water, and the residue (9·8 gms.) dissolved in boiling sodium carbonate (saturated in the cold) and allowed to remain, when the sodium salt of the above acid is gradually deposited as a colourless, crystalline precipitate. This is collected, decomposed by hydrochloric acid, and the acid recrystallised from glacial acetic acid, from which it separates in hair-like prisms which on standing in the solution gradually change to large, yellow prisms, m. p. 258° (Found: C = 68·5; H = 4·8; N = 7·8. $C_{20}H_{16}O_4N_2$ requires C = 69·0; H = 4·6; N = 8·0 per cent.). On acidifying the intensely coloured filtrate from the sodium salt, a blue dye (1·2 gms.) of poor tinctorial value is obtained.

s.-*Diphenyl-o-phenylenediamine.*—The above acid (6 gms.) was heated under reduced pressure, when, after vigorous evolution of carbon dioxide had taken place, a pale yellow syrup (4 gms.) passed over at 280—290°/40 mm. and quickly solidified; it crystallised from a little methyl alcohol in pale, biscuit-coloured prisms, m. p. 109° (Found: C = 83·0; H = 6·2; N = 10·8. $C_{18}H_{16}N_2$ requires C = 83·1; H = 6·1; N = 10·8 per cent.). This substance is a rather weak base; it dissolves in sulphuric acid (50 per cent.) to a colourless solution, and, on the addition of dichromate, a violet coloration develops which gradually changes to a yellowish-brown.

The *diacetyl* derivative, prepared by boiling the base for 4 hours with five times its weight of acetic anhydride, is very soluble in alcohol and crystallises from nitrobenzene–xylene in pale ochre prisms, m. p. 281° (Found: N = 7·6. $C_{22}H_{20}O_2N_2$ requires N = 8·1 per cent.).

s.-Diphenyl-*o*-phenylenediamine does not appear to have been previously described. Wieland (*Ber.*, 1913, **46**, 3303) claims to have prepared it in poor yield (25 per cent.) from *o*-aminodiphenylamine by heating in nitrobenzene solution with iodobenzene and potassium carbonate,

$$NH_2{\cdot}C_6H_4{\cdot}NHPh + PhI \longrightarrow C_6H_4(NHPh)_2,$$

and describes the base as crystallising in colourless pyramids melting at 152·5°, whereas diphenyl-*o*-phenylenediamine melts at 109°. He also gives a list of colour reactions which show clearly that his substance is quite different from that described above. We are of the opinion that Wieland's base (m. p. 152·5°) is *o*-aminotriphenylamine formed according to the scheme:

$$NH_2{\cdot}C_6H_4{\cdot}NHPh + PhI \longrightarrow NH_2{\cdot}C_6H_4{\cdot}NPh_2.$$

Recently, Piccard and Brewster (*J. Amer. Chem. Soc.*, 1921, **43**, 2630) have prepared *o*-aminotriphenylamine by reduction of the corresponding nitro-derivative and describe it as melting at 145°,

which is rather lower than the melting point of Wieland's base; they also state that the acetyl derivative melts at 130°. Identity will be established when the base prepared by Wieland's method is converted into the acetyl derivative, which, so far, has not been done.

6-Carboxydiphenylamine-2'-aminoacetic Acid and the Anhydro-derivative (IX and X).

The solid bisulphite derivative of formaldehyde,

$$OH{\cdot}CH_2{\cdot}SO_3Na,H_2O$$

(16 gms.), was added to 2'-aminodiphenylamine-6-carboxylic acid (22·5 gms.; p. 1779), dissolved in sodium hydroxide (4 gms.) and water (150 c.c.), and the solution heated on the steam-bath for 3 hours. The product was cooled, potassium cyanide (7·6 gms.) added, again heated for 2 hours on the steam-bath, sodium hydroxide (50 c.c. of 25 per cent.) added, and the whole boiled until the evolution of ammonia had ceased. Sulphur dioxide was then passed into the clear solution, the pale yellow precipitate collected, washed with water, and dried, when the amino-acid, m. p. 195°, was obtained in a yield of 24·5 gms. This acid cannot be conveniently crystallised but, after digesting with alcohol (250 c.c.), the residue (16 gms.) melted at 212° and evidently consisted of the nearly pure aminoacetic acid (Found: C = 62·3; H = 5·0; N = 9·8. $C_{15}H_{14}O_4N_2$ requires C = 62·9; H = 5·0; N = 9·8 per cent.). The suspension of this substance in sulphuric acid (50 per cent.) gives a violet coloration on the addition of dichromate.

Ethyl Anhydro-6-carboxydiphenylamine-2'-aminoacetate.—When hydrogen chloride was passed for 2 hours into absolute alcohol (500 c.c.) and the aminoacetic acid (25 gms.) at 0°, a colourless hydrochloride was produced. The mixture was left for 24 hours and then heated under reflux for 24 hours on the steam-bath, when a clear red solution was obtained.

The alcohol was distilled off under reduced pressure, and the last traces were removed by distillation in steam, during which an oil separated which gradually solidified. The solid was collected and ground with weak ammonia; it then weighed 22·5 gms., melted at about 135°, and separated from alcohol in pale yellow prisms which softened at 146° and melted at 152—153° (Found: C = 68·9; H = 5·4; N = 9·5. $C_{17}H_{16}O_3N_2$ requires C = 68·9; H = 5·4; N = 9·4 per cent.). This substance dissolves in sulphuric acid (50 per cent.) to a pale yellow solution, which becomes reddish-brown on the addition of dichromate.

The Nitroso-derivative.—A solution of the crude anhydro-ester just described (39 gms.) in acetic acid (250 c.c.) is cooled in ice-

water, and hydrochloric acid (65 c.c.) and ice are added. Aqueous sodium nitrite (13 gms.) is gradually run in with cooling and stirring, and the product diluted with water (500 c.c.), when a gum separates which slowly solidifies. This crude nitroso-derivative is purified by grinding with very dilute sodium hydroxide solution, it is then collected, washed with water, and dried, when it weighs 35 grams and melts at about 100°. It crystallises from alcohol in stout, pale yellow prisms, m. p. 117° (Found : C = 63·0; H = 4·7; N = 12·9. $C_{17}H_{15}O_4N_3$ requires C = 62·8; H = 4·6; N = 12·9 per cent.). The reduction of this substance and its condensation with *cyclo*hexanone are described in the next section.

Anhydro-8-o-*carbethoxyphenylamino*-1 : 2 : 3 : 4-*tetrahydrocarbazole*-9-*acetic Acid* (XII).—A solution of the preceding crude powdered nitroso-derivative (18 gms.) in warm glacial acetic acid (90 c.c.) is cooled to 30°, mixed with *cyclo*hexanone (15 c.c.), and then zinc dust (30 gms. of 90 per cent.) added in small portions, with vigorous stirring and shaking during 10 minutes, so that the temperature remains at 40—45°. The stirring is continued for a further 10 minutes at 45°, the mixture filtered, the zinc residue extracted with warm acetic acid, and the combined filtrates heated for about 15 minutes on the steam-bath. If the solution is now cooled, the crystalline ester separates, but the better plan is to add water (300 c.c.), collect the solid, and grind it with alcohol (25 c.c.), which removes some impurity and leaves 14·2 gms. of the nearly pure ester. *Anhydro-carbethoxyphenylaminotetrahydrocarbazoleacetic acid* separates from alcohol, in which it is sparingly soluble, in long, pale yellow prisms, m. p. 171—172° (Found : C = 73·7; H = 6·1; N = 7·2. $C_{23}H_{22}O_3N_2$ requires C = 73·8; H = 5·9; N = 7·5 per cent.).

8-o-*Carboxyphenylamino*-1 : 2 : 3 : 4-*tetrahydrocarbazole*-9-*acetic Acid* (p. 1756).—The ester just described (3 gms.) is hydrolysed by boiling with methyl alcoholic potassium hydroxide (50 c.c. of 20 per cent.) and methyl alcohol (25 c.c.) for 3 hours. The bulk of the methyl alcohol is removed by distillation under reduced pressure, water added, sulphur dioxide passed into the cold solution and, after ½ hour, the precipitated acid is collected, dried, and crystallised from much methyl alcohol, from which it separates in pale yellow prisms, m. p. 243° (decomp.) (Found : C = 68·9; H = 5·6; N = 7·6. $C_{21}H_{20}O_4N_2$ requires C = 69·2; H = 5·5; N = 7·7 per cent.).

The *acetyl* derivative, readily produced when the dibasic acid is boiled with glacial acetic acid, separates, on cooling, in dull yellow prisms, m. p. 250° (decomp.) (Found : C = 68·1; H = 5·5; N = 7·1. $C_{23}H_{22}O_5N_2$ requires C = 68·0; H = 5·4; N = 6·9 per cent.).

Anhydrocarboxyphenylaminotetrahydrocarbazoleacetic Acid.

The preceding dibasic acid (2 gms.) is heated on the steam-bath for 15 minutes with sulphuric acid (14 c.c. of 95 per cent.), the product poured on to ice, the whole heated to boiling, and the yellow precipitate (1·5 gms.) collected and thoroughly washed with water. The dry substance is extracted with alcohol (20 c.c.), when a trace of a yellow substance insoluble in sodium hydroxide remains.

The alcoholic solution is basified with sodium hydroxide, filtered, acidified with acetic acid, and the precipitated acid washed with water and dried (Found: C = 72·4; H = 5·3; N = 7·7. $C_{21}H_{18}O_3N_2$ requires C = 72·8; H = 5·2; N = 8·1 per cent.).

This acid shrinks at 200°, melts at about 255°, and is soluble in dilute sodium hydroxide to a pale yellow solution which exhibits a blue fluorescence.

The *ethyl* ester is obtained when the anhydro-acid (2 gms.), suspended in alcohol (20 c.c.), is saturated with hydrogen chloride and the whole heated to boiling in a reflux apparatus for 24 hours. On adding ice, the nearly pure ester separates as a pale yellow precipitate which unfortunately cannot be recrystallised. It is ground with dilute sodium hydroxide, dissolved in alcohol, and the filtered solution mixed with brine, when the colloidal liquid deposits an amorphous precipitate which, after washing and drying over sulphuric acid, yields the correct analytical numbers (Found: C = 73·7; H = 6·0. $C_{23}H_{22}O_3N_2$ requires C = 73·8; H = 5·9 per cent.).

9-*Nitrothioacridone* (XIV).

9-Nitroacridone (p. 1770; 6 gms.) was well mixed with freshly distilled phosphorus pentasulphide (6 gms.) and heated in a large test tube in an oil-bath, which was stirred and kept at 140°. Several such tubes were heated in one operation and each tube was withdrawn every 5 minutes, well stirred, replaced, and the temperature gradually raised to 160° during 1 hour and then to 170° during 30 minutes. The brick-red product was extracted with boiling xylene, from which 9-*nitrothioacridone* separated in brilliant, almost black prisms which, after recrystallisation, melted at 236° (Found: C = 61·0; H = 3·1; N = 10·8. $C_{13}H_8O_2N_2S$ requires C = 60·9; H = 3·1; N = 10·9 per cent.). When suspended in alcohol and reduced by sodium amalgam in presence of sodium bicarbonate, under the conditions described in the next section, 9-nitrothioacridone yields 9-amino-5 : 10-dihydroacridine.

Reduction of 9-*Nitroacridone to* 9-*Amino*-5 : 10-*dihydroacridine* (XIII).—9-Nitroacridone (80 gms.), sodium hydrogen carbonate (380 gms.), and alcohol (2300 c.c. of 90 per cent.) were placed in a

3-litre flask fitted up as described on p. 1772. The flask was heated in a water-bath at 65—70°, the contents well stirred, and a steady stream of carbon dioxide passed while sodium amalgam (2550 gms. of 4 per cent.) was added during 1—2 hours, care being taken that the temperature did not rise above 70°. When all the amalgam had been added, the temperature was raised so that the alcohol boiled slowly for an hour, the mixture was then allowed to cool slowly to about 50°, the stirring and passage of carbon dioxide being continued all the time. The alcoholic solution was filtered, the residual sodium carbonate washed with warm alcohol, the combined filtrates concentrated by distillation under reduced pressure to about 300 c.c. and then added, with stirring, to cold water (1500 c.c.). The almost colourless precipitate was collected, well pressed, and dried overnight in a vacuum desiccator over sulphuric acid, when 60—64 gms., melting at 104—108°, were obtained (theor. yield 65·3 gms.). This crude aminodihydroacridine is pure enough for most purposes, but the substance may be recrystallised from light petroleum,* from which it separates in thin, colourless needles, m. p. 114° (Found: C = 79·8; H = 6·1; N = 14·1. $C_{13}H_{12}N_2$ requires C = 79·6; H = 6·1; N = 14·3 per cent.).

9-*Amino*-5 : 10-*dihydroacridine* is readily soluble in alcohol, ether, acetone, or acetic acid. It dissolves in dilute hydrochloric acid, but the solution in acetic acid is dissociated on the addition of water. The addition of a trace of dichromate to the deep yellow solution in concentrated sulphuric acid causes an intense green fluorescence to develop.

9-*Acetylamino*-5 : 10-*dihydroacridine and* 9-*Acetylaminoacridine*.—A solution of aminodihydroacridine (10 gms.) in acetic anhydride (20 c.c.) is heated on the steam-bath for 15 minutes, and the *acetylaminodihydroacridine* is precipitated by water and recrystallised from methyl alcohol, from which it separates in slightly brown plates, m. p. 177° (Found: C = 75·9; H = 6·0. $C_{15}H_{14}ON_2$ requires C = 75·6; H = 5·9 per cent.).

A mixture of this substance (10 gms.) and acetic acid (120 c.c.) is heated on the steam-bath while potassium dichromate (5 gms. in hot water, 20 c.c.) is gradually run in. The deep red-brown solution is heated for 15 minutes, and diluted with hot water, when an oil is obtained which soon crystallises (10 gms.; m. p. 105—110°). The solid is extracted with ether, when rather less than a gram of a brown impurity remains undissolved, and, after removal of the ether, the 9-*acetylaminoacridine* is recrystallised from light petroleum, from

* During the crystallisation from light petroleum, in which the substance is not very soluble, a certain amount of oxidation occurs, since some 9-aminoacridine crystallises from the mother-liquors after concentration.

which it separates in yellow needles, m. p. 117° (Found: C = 76·1; H = 5·2. $C_{15}H_{12}ON_2$ requires C = 76·3; H = 5·1 per cent.).

9-*Aminoacridine.*—The acetyl derivative was hydrolysed by boiling with dilute sulphuric acid (60 per cent.) for an hour, diluting, neutralising, and extracting the base, which separated, with ether. After removal of the ether, the 9-aminoacridine was crystallised from light petroleum (b. p. 80—100°), from which it separated in stout, orange prisms, m. p. 105—106° (Found: C = 80·4; H = 5·4. $C_{13}H_{10}N_2$ requires C = 80·4; H = 5·2 per cent.). This base dissolves with difficulty in sulphuric acid (50 per cent.) and the addition of dichromate produces a dull violet coloration which changes to a port wine colour on dilution.

The *hydrochloride* separates from dilute alcohol in yellow needles, m. p. 234° (decomp.).

Acridine-9-aminoacetic Acid (XVI).

9-Aminoacridine condenses with chloroacetic ester when the mixture is digested in alcoholic solution in presence of sodium acetate for 48 hours. After distilling off the alcohol under reduced pressure and adding water, ethyl acridine-9-aminoacetate is obtained and separates from light petroleum in pale brown prisms, m. p. 108—109° (Found: C = 72·9; H = 5·8; N = 10·0. $C_{17}H_{16}O_2N_2$ requires C = 72·9; H = 5·7; N = 10·0 per cent.). *Acridine-9-aminoacetic acid* is obtained from this ester by hydrolysis with methyl-alcoholic potassium hydroxide and crystallises from methyl alcohol in small, brownish-red prisms, m. p. about 185° (decomp.) (Found: C = 71·1; H = 4·8; N = 11·0. $C_{15}H_{12}O_2N_2$ requires C = 71·4; H = 4·8; N = 11·1 per cent.). The *nitroso*-derivative of ethyl acridine-9-aminoacetate is readily prepared in the usual way (ester 5 gms., cold acetic acid 85 c.c., water 12 c.c.; sodium nitrite 7·5 gms., water 35 c.c.). The reddish-brown solid obtained on dilution with water is washed, dried in a vacuum desiccator over sulphuric acid, and crystallised from acetone, from which it separates in dull grey needles, m. p. 115—117° (Found: C = 66·2; H = 4·8; N = 13·8. $C_{17}H_{15}O_3N_3$ requires C = 66·0; H = 4·8; N = 13·6 per cent.).

It is remarkable that this nitroso-derivative behaves differently from other similarly constituted substances described in this communication in that it does not appear to yield a condensation product when it is reduced by zinc dust and acetic acid in presence of *cyclo*hexanone.

Apparently the nitroso-group is eliminated under these conditions, since the only substance which could be isolated from the product of the reduction was acridine-9-aminoacetic ester.

9-*Ethylaminoacridine*, $C_{13}H_8N{\cdot}NHEt$ (XXVI).—The toluene-*p*-sulphonyl derivative of 9-aminoacridine, $C_{13}H_8N{\cdot}NH{\cdot}SO_2{\cdot}C_6H_4Me$, readily prepared by adding toluene-*p*-sulphonyl chloride and sodium acetate to the alcoholic solution of the base (for details, compare p. 1791), crystallises from boiling alcohol, in which it is sparingly soluble, in colourless, rhombic plates, m. p. 169—170° (Found: C = 69·0; H = 4·6. $C_{20}H_{16}O_2N_2S$ requires C = 69·0; H = 4·6 per cent.). It is hydrolysed by boiling with dilute sulphuric acid (60 per cent.) for 4 hours and the yield of 9-aminoacridine obtained is almost quantitative. The sulphonyl derivative dissolves in concentrated hydrochloric acid or a mixture of acetic acid and hydrochloric acid, but the hydrochloride soon separates in brownish-yellow rhombs, m. p. 242° (decomp.) It also dissolves readily in alcohol containing sodium hydroxide and, on standing, the sodium derivative gradually separates in long prisms with pointed ends. The ethylation of the toluene-*p*-sulphonyl derivative was carried out by warming the substance (30 gms.) with alcohol (400 c.c.) and *N*-sodium hydroxide (100 c.c.) until solution was complete. Ethyl toluene-*p*-sulphonate (18 gms.) was then added, the liquid kept at 60—70° for 3 hours, boiled for an hour, and left over-night. The pale brown, crystalline deposit (25 gms.) was boiled with alcohol (400 c.c.) containing 2*N*-sodium hydroxide (40 c.c.), and the whole cooled and filtered. This treatment removed the un-alkylated material and left a crystalline product (12 gms.), which separated from alcohol, in which it was rather sparingly soluble, in colourless, flat needles, m. p. 175—176° (Found: C = 70·4; H = 5·5. $C_{22}H_{20}O_2N_2S$ requires C = 70·2; H = 5·3 per cent.).

9-*Ethylaminoacridine*.—The sulphonyl derivative just described (12 gms.) was dissolved in sulphuric acid (200 c.c. of 60 per cent.), the greenish-yellow solution was gently boiled for 5 hours, cooled with ice, neutralised with sodium hydroxide, and the precipitated reddish-orange solid extracted with ether. On evaporating off the ether, a deep red oil remained in almost quantitative yield and this quickly solidified. 9-*Ethylaminoacridine* separates from light petroleum, in which it is readily soluble, in large, orange-red, rhombic plates, m. p. 65°. It appears to be dimorphic and sometimes separates in unstable, long, golden prisms (Found: C = 81·1; H = 6·3. $C_{15}H_{14}N_2$ requires C = 81·1; H = 6·3 per cent.). The yellow solution in concentrated sulphuric acid exhibits an intense green-yellow fluorescence and the addition of dichromate changes the colour to deep blue-violet.

It is remarkable that the solution in dilute sulphuric acid (50 per cent.) does not exhibit any fluorescence.

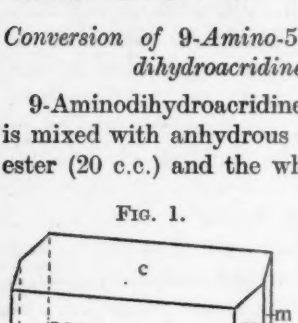
9-*Acetylethylaminoacridine*.—When the base is heated with acetic

anhydride on the steam-bath, the deep red solution formed at first soon changes to light yellow. Water is now added, to decompose the excess of anhydride, and the solution made just alkaline with sodium hydroxide, when a syrup separates which rapidly crystallises and colourless, hexagonal plates form in the aqueous solution. The *acetyl* derivative separates from light petroleum in stout, colourless, hexagonal plates, m. p. 95° (Found : C = 76·7; H = 6·3. $C_{17}H_{16}ON_2$ requires C = 77·3; H = 6·0 per cent.).

Conversion of 9-*Amino*-5 : 10-*dihydroacridine into Anhydro*-5 : 10-*dihydroacridine*-9-*aminoacetic Acid* (XXIII).

9-Aminodihydroacridine* (20 gms.), dissolved in alcohol (200 c.c.), is mixed with anhydrous sodium acetate (20 gms.) and chloroacetic ester (20 c.c.) and the whole boiled under reflux for 3 days. The product, cooled and kept at 0°, is saturated with hydrogen chloride, again heated on the steam-bath for 24 hours, the red solution is then poured into water (1·5 litres) and left over-night. The dark red, pasty mass which will have separated is rubbed with a little methyl alcohol, the solid collected and washed with methyl alcohol until the filtrate is almost colourless, when the practically pure anhydro-derivative (13 gms.) remains; after drying, it melts at 166—167°. The substance may then be further purified by crystallisation from alcohol (Found : C = 76·4; H = 5·3; N = 11·5. $C_{15}H_{12}ON_2$ requires C = 76·3; H = 5·1; N = 11·8 per cent.).

FIG. 1.



Anhydrodihydroacridine-9-*aminoacetic acid* melts at 168° and crystallises in two forms. When the hot concentrated alcoholic solution is rapidly cooled, the unstable form separates in very pale yellow, thin prisms and, on standing, these are gradually converted into the stout, deep yellow prisms of the stable variety. We are indebted to Mr. T. V. Barker for the following description of the crystals of the stable variety.

The crystals belong to the monoclinic system and exhibit the following forms : *a*{100}, *c*{001}, and *m*{110}. They show a habit elongated parallel to the *b*-axis (see Fig. 1) and tabular parallel to *a*{100}. The faces of the crystals are curved and therefore give bad reflections. Three crystals were measured. The mean results of measurement for *c*{001} are : azimuth (ϕ) = 89° 21′; polar distance

* The crude substance melting at 104—108° (p. 1785) may be employed with advantage, but any material of less purity must not be used; otherwise the experiment may easily fail completely.

$(\rho) = 24°\ 23'$: for $m\{110\}$, azimuth $(\phi) = 15°\ 11'$; polar distance $(\rho) = 90°\ 5'$. Axial ratio $a : b = 4{\cdot}046 : 1$, $\beta = 114°\ 23'$. The optic axial plane is perpendicular to the plane of symmetry and the acute bisectrix emerges inclined through $a\{100\}$.

The addition of a little solid dichromate to the solution of this substance in concentrated sulphuric acid produces a deep reddish-brown coloration with a tinge of violet. It yields an intense red solution on dissolving in concentrated nitric acid. The *acetyl* derivative is readily produced when the substance is digested with acetic anhydride and separates from alcohol in colourless prisms, m. p. 174—175° (Found : N = 10·1. $C_{17}H_{14}O_2N_2$ requires N = 10·1 per cent.).

The *nitroso*-derivative may be prepared by dissolving crude anhydrodihydroacridine-9-aminoacetic acid (10 gms.) in warm acetic acid (62 c.c.) and hydrochloric acid (16 c.c.), cooling below 10°, and gradually adding sodium nitrite (4 gms.) in water (16 c.c.). A pale biscuit-coloured precipitate separates and, after stirring for 15 minutes, this is collected, ground with dilute sodium carbonate, well washed with water, and dried on the steam-bath. The product (10·5 gms.) crystallises from boiling alcohol, in which it is rather sparingly soluble, in bright yellow prisms which, when rapidly heated, melt at 167° with decomposition (Found : N = 15·7. $C_{15}H_{11}O_2N_3$ requires C = 15·9 per cent.).

Action of Phosphorus Pentachloride on Anhydro-5 : 10-dihydroacridine-9-aminoacetic Acid.

The acid (9·5 gms.), dissolved in dry chloroform (80 c.c.), was cooled in ice and water, and phosphorus pentachloride (12 gms.) added in small portions with shaking, when the solution became dull red. After stirring and warming at 40° during 15 minutes, the chloroform was removed by distillation under reduced pressure and the residue mixed with ice and water. The solid which separated was collected, ground with dilute sodium hydroxide, and dissolved in boiling glacial acetic acid, in which it was sparingly soluble and from which colourless prisms, m. p. 175—178° (decomp.), gradually separated (Found : Cl = 6·0; N = 8·8. $C_{30}H_{23}O_3N_4ClP$ requires Cl = 6·3; N = 10·0 per cent.). This curious substance was hydrolysed by boiling with methyl-alcoholic potassium hydroxide and the anhydro-derivative, from which it had been prepared, was regenerated.

11 : 12-*Dihydroacridoxaline* (XXV).

This substance was obtained by the electrolytic reduction of a cold (brownish-red) solution of anhydro-5 : 10-dihydroacridine-9-

acetic acid (6 gms.) in dilute sulphuric acid (160 c.c. of 60 per cent.) in the apparatus described on p. 1798, a current of 6 amps. being passed for about 15 hours. The colourless solution, containing a considerable colourless precipitate of a sulphate, was poured into ice and water, the precipitate collected, washed with water, and dried in a vacuum desiccator (5·6 gms.). This sulphate dissolved in concentrated sulphuric acid to a colourless solution which exhibited an intense pale green fluorescence, and a deep purple coloration was produced on the addition of potassium dichromate. The sulphate was ground with dilute ammonia, when a pale yellow, viscous base (5 gms.) was obtained which could not be crystallised and, on account of its extremely irritant action on the skin, was very unpleasant to work with. The base was extracted with ether, the ethereal solution dried over potassium carbonate and evaporated, when a gum remained which, after some weeks, showed some sign of crystallising.

It was then found that the crude base may be readily purified by converting it into the *acetyl* derivative by heating it (3·5 gms.) with acetic anhydride (12 c.c.) for 1 hour on the steam-bath and adding hot water; after cooling, the colourless solid was ground with dilute sodium carbonate, washed, and dried.

Acetyl-11 : 12-*dihydroacridoxaline* separates from methyl alcohol, in which it is rather readily soluble, in stout, well-developed, colourless prisms, m. p. 152° (Found : C = 77·3; H = 6·1; N = 10·4. $C_{17}H_{16}ON_2$ requires C = 77·3; H = 6·0; N = 10·6 per cent.). When this acetyl derivative was hydrolysed by boiling with methyl-alcoholic potassium hydroxide, the irritant base was again obtained as a sticky, nearly colourless mass. This dissolved very readily in methyl alcohol to a nearly colourless solution which, on standing in the air, quickly became deep purple. As the base could not be crystallised, it was distilled under reduced pressure and the brittle orange resin analysed (Found : C = 80·0; H = 6·3; N = 10·7. $C_{15}H_{14}N_2$ requires C = 81·1; H = 6·3; N = 12·6 per cent.). That this resin consists essentially of 11 : 12-*dihydroacridoxaline* was proved by the fact that, when it was heated with acetic anhydride, it yielded a considerable quantity of the acetyl derivative melting at 152°. It is curious that attempts to obtain a nitroso-derivative of this base have not been successful. On two occasions, however, a small amount of a crystalline substance was obtained which separated from methyl alcohol in well-defined, bright yellow prisms, m. p. 125°, but the analytical results did not agree with those required for the nitroso-derivative (Found : C = 73·6; H = 5·2; N = 15·8. $C_{15}H_{13}ON_3$ requires C = 71·7; H = 5·2; N = 16·7 per cent.).

*The Toluene-*p*-sulphonyl Derivative of 9-Amino-5 : 10-dihydroacridine* (p. 1758) *and its Derivatives.*

This toluene-*p*-sulphonyl derivative was prepared by dissolving aminodihydroacridine (27 gms.; m. p. 104—108°; p. 1785) in alcohol (130 c.c.) * and adding sodium acetate (54 gms.) and toluene-*p*-sulphonyl chloride (40·5 gms.). On vigorously shaking the mixture for a minute, the whole set to a pale biscuit-coloured mass and there was some rise of temperature. After the solution had been concentrated somewhat, the precipitate was collected, washed with hot water, dried (47 gms.), and crystallised from boiling alcohol (1250 c.c.), from which it separated in bright yellow, well-defined, stout prisms, m. p. 190—191° (Found : C = 68·3; H = 5·1. $C_{20}H_{18}O_2N_2S$ requires C = 68·6; H = 5·1 per cent.). This substance is readily soluble in hot dilute aqueous sodium hydroxide.

The β-*chloroethyl* derivative (XVII) was prepared by dissolving the toluene-*p*-sulphonyl derivative (21 gms.) in alcohol (200 c.c. of 95 per cent.) and sodium hydroxide (15 c.c. of 22·5 per cent.); β-chloroethyl toluene-*p*-sulphonate (24 gms.) was then added and the whole heated in a water-bath at 75—78° for 4 hours. A further quantity of the β-chloroethyl sulphonate (8 gms.) was then added, the heating continued for 2 hours, and the bulk of the alcohol distilled off. The residue was boiled with dilute sodium hydroxide solution and crystallised from alcohol, when 19·5 gms. were obtained, m. p. about 125—145°. When this crude product was ground, extracted twice with hot dilute sodium hydroxide (4 per cent.), so as completely to remove any unchanged toluene-*p*-sulphonyl derivative of aminodihydroacridine, and then crystallised from alcohol, the pure β-*chloroethyl derivative* of *toluene*-p-*sulphonylamidodihydroacridine* separated in stout, bright yellow prisms, m. p. 147—148° (Found : C = 64·3; H = 5·3; N = 7·0. $C_{22}H_{21}O_2N_2ClS$ requires C = 64·0; H = 5·1; N = 6·8 per cent.). Attempts were made to close the dihydrocarboxaline ring by heating the sulphonyl derivative with diethylaniline, sodium acetate, and acetic anhydride and with methyl-alcoholic potassium hydroxide or dilute sulphuric acid (60 per cent.), but without any success.

The β-*Hydroxyethyl Derivative* (p. 1758).—The toluene-*p*-sulphonyl derivative of aminodihydroacridine (14 gms.), methyl-alcoholic potassium hydroxide (12·8 c.c. of 20 per cent.), ethylene chlorohydrin (6·4 c.c.), and methyl alcohol (20 c.c.) were mixed and heated

* If water is used in the place of alcohol, a product is obtained which crystallises in well-defined, yellow prisms, melts at 155—185°, and gives the same analytical numbers as the substance of m. p. 191°. It also exhibits the same reactions as the substance of m. p. 191° and obviously contains an isomeride of that substance, but the nature of this has not been investigated.

in a sealed tube in the water-bath for 21 hours. The contents of three such tubes were worked up together, the alcohol being removed on the steam-bath, hot dilute sodium hydroxide added, and the pale yellow solid collected. This was finely powdered, twice extracted with boiling dilute sodium hydroxide (4 per cent.), and crystallised from alcohol, the β-*hydroxyethyl* derivative (42 gms.) separating in very pale yellow prisms, m. p. 154—155° (Found: C = 66·6; H = 5·9; N = 7·0. $C_{22}H_{22}O_3N_2S$ requires C = 67·0; H = 5·6; N = 7·1 per cent.). Attempts were made to close the dihydrocarboxaline ring by heating this sulphonyl derivative with phosphoryl chloride or by boiling with dilute sulphuric acid (60 per cent.), but without success. In the latter case a poor yield of 9-β-hydroxyethylaminoacridine resulted, a substance which, it was subsequently found, could be obtained more readily under the conditions described in the next Section.

9-β-*Hydroxyethylaminoacridine* (XVIII).

The toluenesulphonyl derivative of 9-β-hydroxyethylaminodihydroacridine just described (20 gms.) is dissolved in warm acetic acid (125 c.c.), the solution heated on the steam-bath and stirred while a hot solution of potassium dichromate (5·2 gms.) in water (50 c.c.) is run in during 5 minutes.

The heating and stirring are continued for 10 minutes and the deep brownish-yellow solution added to ice, when a hard, granular solid separates which is collected, ground with dilute sodium carbonate, and crystallised from alcohol, from which dull yellow plates (17·4 gms.) separate. This *toluene*-p-*sulphonyl* derivative of 9-β-*hydroxyethylaminoacridine* melts at 156° and is readily hydrolysed with elimination of the toluene-*p*-sulphonyl group, by dissolving the powdered substance (10 gms.) in hot dilute sulphuric acid (110 c.c. of 60 per cent.) and boiling the intensely greenish yellow fluorescent solution in a reflux apparatus for 3½ hours. The resulting dull red solution is cooled, poured on ice, made alkaline with ammonia, and the base extracted with ether, by which means it is separated from a small amount of an insoluble substance.

On removing the ether, a bright yellow solid (4·2 gms.) remains which is crystallised from light petroleum (b. p. 100—120°), in which it is rather sparingly soluble, and from which it separates in long, thin, reddish-orange prisms (Found: C = 75·7; H = 6·0; N = 11·8. $C_{15}H_{14}ON_2$ requires C = 75·6; H = 5·9; N = 11·8 per cent.).

9-β-*Hydroxyethylaminoacridine* melts at 109—110° and dissolves in concentrated sulphuric acid to a greenish-yellow solution exhibiting a striking fluorescence. The solution in sulphuric acid (50 per cent.) is bright yellow and fluoresces only very faintly. The

addition of dichromate produces a deep blue coloration which becomes violet on dilution. The solution in concentrated nitric acid is deep red.

9-β-*Hydroxyethylamino*-5 : 10-*dihydroacridine* (XIX).

This substance is obtained when 9-β-hydroxyethylaminoacridine (see last section) is reduced with sodium amalgam in the apparatus and under the conditions described on p. 1772. The quantities were : β-hydroxyethylaminoacridine (3·6 gms.), sodium bicarbonate (5 gms.), alcohol (60 c.c. of 95 per cent.), and sodium amalgam (60 gms. of 4 per cent.). The almost colourless reduction product which, after drying on the steam-bath weighed 3·7 grams and melted at 120°, was crystallised from methyl alcohol, in which it was readily soluble and from which it gradually separated in stout, pale yellow, flat prisms (Found : C = 74·9; H = 6·8. $C_{15}H_{16}ON_2$ requires C = 75·0; H = 6·7 per cent.).

9-β-*Hydroxyethylaminodihydroacridine* melts at 122—123° and dissolves in sulphuric acid to a colourless solution exhibiting only a very slight pale green fluorescence. The pale yellow solution in dilute sulphuric acid (50 per cent.) is changed by dichromate first to greenish-blue, then to reddish-brown, and on dilution to reddish-violet. The deep red solution in concentrated nitric acid deposits a yellow precipitate on dilution.

The following attempts to close the dihydrocarboxaline ring were unsuccessful : (i) heating with anhydrous formic acid or with phosphorus pentachloride; (ii) digesting for 24 hours with saturated alcoholic hydrochloric acid, after which drastic treatment almost the whole of the substance was recovered unchanged ; (iii) when the substance (1 gm.) was heated with sulphuric acid (5 c.c.) at 60°, oxidation took place, as was evidenced by the liberation of sulphur dioxide, and sulphonation also occurred with the formation of a fine deep red solution which doubtless contained a sulphonic acid of 9-β-hydroxyethylaminoacridine.

The *diacetyl* derivative (p. 1759) is obtained when the base is heated on the steam-bath with three times its weight of acetic anhydride for 1½ hours. After the excess of anhydride has been decomposed by contact with water, the colourless diacetyl derivative is collected and crystallised from methyl alcohol, in which it is rather sparingly soluble and from which it separates in stout, flat prisms, m. p. 148° (Found : C = 70·2; H = 6·5; N = 8·2. $C_{19}H_{20}O_3N_2$ requires C = 70·4; H = 6·2; N = 8·6 per cent.). This diacetyl derivative is decomposed by boiling with methyl-alcoholic potassium hydroxide with regeneration of β-hydroxyethylaminodihydroacridine.

The *monoacetyl* derivative is produced when the diacetyl derivative (3 gms.) is digested in a reflux apparatus with saturated alcoholic hydrogen chloride (75 c.c.) for 24 hours. The magenta-coloured solution is distilled under reduced pressure to remove the bulk of the alcohol, the residue cooled, mixed with ice-cold ammonia, filtered from a small amount of an orange-coloured gum, and excess of sodium hydroxide added. The precipitate, which is sticky at first but soon hardens, is dried in a vacuum desiccator and crystallised first from light petroleum and then from methyl alcohol and is thus obtained in very pale brown cubes, m. p. 147—148°. The mixture with the diacetyl derivative, which melts at the same temperature, melts at 130—140° (Found: C = 72·1; H = 6·3; N = 9·5. $C_{17}H_{18}O_2N_2$ requires C = 72·3; H = 6·4; N = 9·9 per cent.). This acetyl derivative dissolves in sulphuric acid with scarcely any fluorescence but, on warming, a bright green fluorescence gradually develops.

*Action of Bromodimethylacetal on the Potassium Derivative of the Toluene-*p*-sulphonyl Derivative of 9-Amino-5 : 10-dihydroacridine.*

The sulphonyl derivative (7 gms.), methyl alcohol (15 c.c.), methyl-alcoholic potassium hydroxide (6·4 c.c. of 20 per cent.), and bromodimethylacetal (7 gms.) were heated in a sealed tube in the boiling-water bath for 18 hours. The contents of four such tubes were mixed and distilled, to remove the bulk of the methyl alcohol, sodium hydroxide (8 per cent.) was added, and the mixture heated on the steam-bath with frequent shaking. The alkaline solution was decanted from the colourless gum, and the treatment with the sodium hydroxide repeated four times. Finally the substance was crystallised from methyl alcohol, from which the *dimethylacetalylsulphonyl* derivative separated in large, well-defined, faintly yellow cubes (13 gms.) which melted at 121° and were not decomposed at 190° (Found: C = 65·9; H = 6·2; N = 6·4. $C_{24}H_{26}O_4N_2S$ requires C = 65·7; H = 5·9; N = 6·4 per cent.).

On acidifying the alkaline extracts with acetic acid, a pale precipitate (14 gms.) was obtained which melted at about 160—165° and appeared to be the toluene-*p*-sulphonyl derivative of 9-aminoacridine.

The dimethylacetalylsulphonyl derivative (1 gm.) dissolved in saturated alcoholic hydrogen chloride (20 c.c.) to a colourless solution which quickly became intense green and, after about an hour, deep brown. On warming at 45° and pouring on to ice, a tar separated and, after decanting from this, the acid solution gave with ammonia, a voluminous pale yellow precipitate, part of which

was sparingly soluble in alcohol, but the substance could not be crystallised. Again nothing crystalline resulted from attempts made to close the dihydrocarboxaline ring by heating with acetic acid or sulphuric acid under a variety of conditions.

Dimethylacetalyl-9-aminoacridine (XX) *and Dimethylacetalyl-9-amino-5 : 10-dihydroacridine* (XXI).

9-Amino-5 : 10-dihydroacridine (p. 1785; 56 gms.), bromodimethylacetal (72·8 c.c.), anhydrous sodium acetate (49 gms.), a trace of copper, and absolute alcohol (200 c.c.) were digested in a reflux apparatus on the steam-bath for 48 hours. The bulk of the alcohol was distilled off, hot water added, the remainder of the alcohol removed on the steam-bath, the heavy, dark syrup separated, dissolved in methyl alcohol (150 c.c.), and left to stand in a conical open flask for a fortnight. The brown solid (26·5 gms.) which had separated was crystallised from light petroleum (b. p. 80—100°), from which the *dimethylacetal* of *9-aminoacridine* separated in glistening, golden-brown, flat prisms, m. p. 87° (Found : C = 72·1; H = 6·5; N = 9·8. $C_{17}H_{18}O_2N_2$ requires C = 72·3; H = 6·4; N = 9·9 per cent.). This substance dissolves in sulphuric acid and the intense greenish-yellow, fluorescent solution changes, on the addition of ice, to a red solution, the slightly blue tint of which disappears on standing and the colour then becomes pure red.

The Dimethylacetal of 9-Amino-5 : 10-dihydroacridine (XXI).—This substance is obtained by the reduction of the acridine derivative, just described, with sodium amalgam in the apparatus and under the conditions described in detail on p. 1772. The quantities employed were : the acridine derivative (10·2 gms.), sodium bicarbonate (15 gms.), alcohol (150 c.c. of 95 per cent.), and sodium amalgam (80 gms. of 4 per cent.).

During the reduction, the initial deep yellow alcoholic solution became quite colourless; the bulk of the alcohol was then distilled off and water and ice were added, when a gum separated which soon hardened. This was dried in a vacuum desiccator and crystallised from light petroleum (b. p. 80—100°), in which the dimethylacetal of aminodihydroacridine was readily soluble and from which it separated in ill-defined, stout, pale yellow prisms (9·2 gms.), m. p. 63—64° (Found : C = 72·0; H = 7·2. $C_{17}H_{20}O_2N_2$ requires C = 71·8; H = 7·0 per cent.).

This substance dissolves in sulphuric acid to an almost colourless, faintly green-fluorescing solution and, on adding ice, the colour changes first to bluish-purple and then gradually to pure blue.

Anhydro-5 : 10 : 16 : 17 : 18 : 19-*hexahydroacrindoline*-21-*acetic Acid* (XXVII).

This important substance is obtained when the nitroso-derivative of anhydrodihydroacridine-9-aminoacetic acid (p. 1789) is reduced with zinc dust and acetic acid in presence of *cyclo*hexanone.

The finely powdered nitroso-derivative (53 gms.) is rapidly stirred with glacial acetic acid (1 litre) and *cyclo*hexanone (30 c.c.) at 40—45°, zinc dust (100 gms. of 90 per cent.) gradually added, and the stirring is then continued for 10 minutes, the product rapidly filtered (pump), the residual mass washed with acetic acid, and the combined filtrates heated at 65—70° for 20 minutes, during which much of the condensation product separates in pale yellow plates. After standing for some hours, the substance is collected, washed with alcohol, and dried, when the yield, including a little which may be obtained by extracting the zinc residues with benzene, amounts to 38 gms. (Found : C = 80·0; H = 5·7; N = 8·7. $C_{21}H_{18}ON_2$ requires C = 80·3; H = 5·7; N = 8·9 per cent.). *Anhydrohexahydroacrindolineacetic acid* separates from benzene in very thin, pale yellow plates, m. p. 205—206°. This substance dissolves in concentrated sulphuric acid to a colourless solution which, on exposure to air on a watch-glass, gradually changes to intense purple; on standing over-night, a brown precipitate of the sulphate of the original substance separates. The addition of a few drops of concentrated sulphuric acid to the suspension of the substance in cold glacial acetic acid gives a light red solution which is changed to a fine bluish-red on the addition of dichromate. This colour change is very reminiscent of the reaction exhibited by strychnine under similar conditions.

Action of Methyl-alcoholic Potassium Hydroxide on Anhydrohexahydroacrindolineacetic Acid.—The substance (1 gm.) was heated with methyl-alcoholic potassium hydroxide (12 c.c. of 20 per cent.) for 10 minutes, and the greenish-yellow fluorescent solution mixed with much water and acidified with acetic acid. The buff, gelatinous precipitate of *hexahydroacrindolineacetic acid* was collected, thoroughly washed with warm water, and dried over sulphuric acid in a vacuum desiccator (Found : C = 75·8; H = 6·1. $C_{21}H_{20}O_2N_2$ requires C = 75·9; H = 6·0 per cent.). This acid is very soluble in alcohol, is converted into a gum in contact with benzene or light petroleum, and all attempts to crystallise it were unavailing. When heated in a reflux apparatus with alcoholic hydrochloric acid, it is largely converted into the anhydro-derivative from which it had been obtained, but some of it suffers oxidation and ethyl tetrahydroacrindolineacetate (m. p. 172°; compare p. 1800) is formed.

On crystallising the product from benzene, the anhydro-derivative separates first and the concentrated mother-liquors then deposit the ester in well-defined, yellow prisms.

Anhydro-5 : 10-*dihydroacridine*-9-*aminodiacetic Acid* (XXIV).

The ester of this acid was obtained in a series of experiments on the action of bromoacetic ester on 9-amino-5 : 10-dihydroacridine (compare p. 1761). The latter substance (4·5 gms.), dissolved in absolute alcohol (60 c.c.), was digested in a reflux apparatus with bromoacetic ester (6·6 c.c.) for 24 hours. The alcohol was distilled off under reduced pressure and the residue crystallised from alcohol, in which it was sparingly soluble and from which the ester separated in very pale yellow prisms, m. p. 154—156° (Found : C = 70·6; H = 5·7; N = 8·7. $C_{19}H_{18}O_3N_3$ requires C = 70·8; H = 5·6; N = 8·7 per cent.). The substance dissolves in concentrated sulphuric acid to a pale yellow solution and an intense reddish-violet colour develops on the addition of solid dichromate.

In order to obtain the free acid, the ester (3 gms.), suspended in methyl alcohol (45 c.c.), was digested with methyl-alcoholic potassium hydroxide (15 c.c. of 20 per cent.) for ½ hour, the methyl alcohol removed by distillation under reduced pressure, and the residue dissolved in water. On acidifying, a gum separated, but this crystallised in contact with methyl alcohol and pure *anhydrodihydroacridine-aminodiacetic acid* separated in glistening prisms when this substance was crystallised from this solvent. These crystals contain methyl alcohol of crystallisation which is lost at 100°; the anhydrous acid melts at 192°. Analysis : (i) 0·1062 lost 0·0108 at 100°, whereas this amount of a substance, $C_{17}H_{14}O_3N_2$,MeOH, should lose 0·0105 MeOH. (ii) The anhydrous substance contained C = 69·3; H = 4·8; N = 9·3, whereas the formula $C_{17}H_{14}O_3N_2$ requires C = 69·4; H = 4·8; N = 9·5 per cent.).

Anhydro-5 : 10-*dihydroacridine*-9-*methylaminoacetic Acid*.—When the above acid is heated in a small distillation flask under a pressure of 20 mm., evolution of carbon dioxide occurs and a pale yellow syrup distils which immediately solidifies, the yield being nearly quantitative.

This methyl derivative (p. 1761) separates from methyl alcohol in very pale yellow plates, m. p. 131—132° (Found : C = 76·5; H = 5·7. $C_{16}H_{14}ON_2$ requires C = 76·8; H = 5·6 per cent.). The solution of this substance in concentrated sulphuric acid has a pale brown colour which is changed to deep reddish-brownish-violet on the addition of dichromate.

21-β-*Hydroxyethyl*-5 : 10 : 15 : 16 : 17 : 18 : 19 : 20-*octahydroacrindoline* (XXX).

This substance is obtained when anhydrohexahydroacrindoline-21-acetic acid (p. 1796) is reduced electrolytically. The cell consisted of a stout beaker of 600 c.c. capacity and internal diameter 7·5 cm. and a cylindrical lead cathode, 2 mm. thick, which roughly fitted around the inside of the beaker. A strip of lead about 2·5 cm. wide and 2 mm. thick formed the anode and was placed in a cylindrical porous cell of about 4·5 cm. external diameter. All the electrolytic reductions described in this communication were carried out in an apparatus of this type at 35—45°, and before each reduction the cathode was coated with a layer of pure lead by placing dilute sulphuric acid (20 per cent.) in the beaker and passing a current of 5 amps. for about 3 hours so as to coat the surface of the lead cylinder with lead peroxide. The weak acid was then replaced by 60 per cent. sulphuric acid and the same current passed for 4—5 hours; the lead cylinder, being now the cathode, became covered with a layer of electrolytic lead.

In the present instance, anhydrohexahydroacrindolineacetic acid (5 gms.) was suspended in alcohol (100 c.c. of 95 per cent.) and sulphuric acid (70 c.c. of 95 per cent.) gradually added, with shaking, until a deep orange solution was obtained. This was placed in the cathode compartment of the electrolytic cell, sulphuric acid of 50 per cent. being in the porous cell, and a current of 6 amps. was passed for 15 hours, when it was noticed that towards the end of the operation the colour of the solution had changed from deep orange to very pale yellow.

The solution was now poured on to ice and water, the pale buff, flocculent precipitate collected, ground with dilute ammonia, washed with water, and dried in a vacuum desiccator, when a brown, amorphous mass remained (1·3—2·5 gms. *A*). The acid filtrate was mixed with ice, made alkaline with ammonia, and the resulting orange-coloured, flocculent precipitate collected, washed with water, and dried in a vacuum desiccator (1·8—3·7 gms. *B*). Repeated attempts to obtain crystalline substances from either (*A*) or (*B*) have always been unsuccessful.

The substance (*B*) was then dissolved in dilute acid and fractionally precipitated with ammonia into a small fraction, a second fraction consisting of the bulk of the material, and a final small fraction.

The second fraction was well washed with water and dried in a vacuum desiccator (Found : C = 79·3; H = 7·5; N = 8·6. $C_{21}H_{24}ON_2$ requires C = 78·7; H = 7·5; N = 8·7 per cent.). There can be little doubt that this substance is almost pure β-*hydroxy*-

ethyloctahydroacrindoline. Subsequently it was discovered that treatment with acetic anhydride converts (*B*) into a crystalline diacetyl derivative.

The substance (10 gms.) was heated with acetic anhydride (50 c.c.) for 2½ hours in the water-bath and water was then added; a brown gum separated which slowly hardened. This was collected, washed with water, and dissolved in a little boiling methyl alcohol, when, on standing, the orange solution very gradually deposited stout, faintly straw-coloured prisms (Found: C = 73·6; H = 7·0; N = 6·7. $C_{25}H_{28}O_3N_2$ requires C = 73·9; H = 6·9; N = 6·9 per cent.).

The *diacetyl* derivative of β-*hydroxyethyloctahydroacrindoline* (XXXI) melts at 235°, and dissolves in sulphuric acid, yielding a colourless solution which does not exhibit fluorescence. When it is hydrolysed by methyl-alcoholic potassium hydroxide, oxidation evidently occurs (compare p. 1764) and the buff precipitate obtained on adding water is probably the corresponding acridine derivative—β-hydroxyethylhexahydroacrindoline—since it dissolves in sulphuric acid to yield a greenish-yellow, intensely fluorescent solution. If the diacetyl derivative is heated in a reflux apparatus with alcoholic hydrochloric acid for 24 hours, the solution yields, on concentration, a pale brown mass which, on treatment with dilute ammonia, is converted into a biscuit-coloured substance. This did not crystallise and was not further examined.

The substance (*A*) yields, on treatment with acetic anhydride, the diacetyl derivative of melting point 235°, and there can therefore be little doubt that the product of the electrolytic reduction of anhydrohexahydroacrindoline consists mainly of β-hydroxyethyloctahydroacrindoline.

10 : 21-*Etheno*-5 : 10 : 16 : 17 : 18 : 19-*hexahydroacrindoline* (XXXII).

Molten anhydrohexahydroacrindoline-21-acetic acid (p. 1796; 3 gms.) was intimately mixed with zinc dust (9 gms. of 90 per cent.) in a hard glass tube and carefully heated under 20 mm. pressure, when a viscid, yellow oil passed over and at once solidified in the receiver (2·6 gms., m. p. about 185°). This product was powdered and the distillation with zinc dust repeated exactly as before. In one series of experiments, 30 gms. of the initial material yielded 24 gms. of distillate after the second distillation, and the powdered substance melted at about 176—181°. This dissolved in benzene to a yellow solution having an intense green fluorescence. This solution was heated with methyl-alcoholic potassium hydroxide (60 c.c. of 20 per cent.) and methyl alcohol (60 c.c.) under reflux

for 1 hour. The benzene and methyl alcohol were removed by distillation, hot water was added, and the alkaline yellow fluorescent solution (*A*) filtered from a pale yellow solid, which, when dry, weighed 12 grams and melted at 178—180°. Finally the substance was crystallised from a small quantity of benzene (Found: C = 84·2; H = 6·2; N = 9·5. $C_{21}H_{18}N_2$ requires C = 84·6; H = 6·0; N = 9·4 per cent.). *Ethenohexahydroacrindoline* melts at 181—182° and is readily soluble in benzene, yielding a yellow solution which exhibits a striking green fluorescence. It separates from benzene in characteristic, long, thin, bright canary-yellow prisms and from alcohol in yellow plates. It dissolves in, but is not changed by, boiling methyl-alcoholic potash. Intensely red, sparingly soluble crystalline salts are obtained when the substance is mixed with concentrated hydrochloric acid or dilute sulphuric acid and, if dichromate is added, deep brown solutions result. The substance dissolves in much concentrated sulphuric acid, the solution exhibiting a striking yellow green fluorescence. It was recovered unchanged after its solution in dilute sulphuric acid (50 per cent.) had been heated for 15 minutes on the boiling-water bath, during which most of the substance gradually separated as the sparingly soluble, red, crystalline sulphate.

16 : 17 : 18 : 19-*Tetrahydroacrindoline*-21-*acetic Acid and its Ester* (XXVIII).

This acid is contained in the yellow, fluorescent filtrate (A., see above) and, on acidifying with acetic acid, separates as a voluminous, light brown, amorphous precipitate which, after drying in a vacuum desiccator, weighs about 11·4 gms. As the crude substance could not be crystallised, it was dissolved in absolute alcohol (150 c.c.), cooled in ice water, saturated with hydrogen chloride, and heated in a reflux apparatus for 24 hours. Much of the alcohol was removed by distillation under reduced pressure, excess of warm dilute sodium hydroxide added, and the brown solid (8 gms.) collected, dried, and extracted with boiling light petroleum (b. p. 100—120°). The filtered solution deposited, on standing, orange prisms (5·5 gms.) of *ethyl tetrahydroacrindoline*-21-*acetate* which, after recrystallisation, melted at 172° (compare p. 1796) (Found: C = 76·7; H = 6·3; N = 8·0. $C_{23}H_{22}O_2N_2$ requires C = 77·1; H = 6·2; N = 8·1 per cent.). The yellow solution of this substance in benzene has an intense green fluorescence.

It is remarkable that, if the above ester is twice distilled with zinc dust (compare p. 1799), the distillate boiled with dilute methyl alcoholic potassium hydroxide, and then water added, a solid separates from which ethenohexahydroacrindoline (m. p. 181°) is

obtained on crystallisation from benzene. The yield is, however, only a small one.

10 : 21-*Ethano*-5 : 10 : 15 : 16 : 17 : 18 : 19 : 20-*octahydroacrindoline* (XXXIV).

The ethenohexahydro-derivative (XXXII; 6 gms.), sodium hydrogen carbonate (12 gms.), and alcohol (200 c.c. of 95 per cent.) were reduced by sodium amalgam (200 gms. of 4 per cent.) in the apparatus and under the conditions described on p. 1772. After 5 hours, the bulk of the alcohol was distilled off under reduced pressure, water added, the pale yellow solid collected, washed, dried (6 gms.), and crystallised from benzene, in which it was much less soluble than (XXXII) and from which it separated in pale yellow prisms, m. p. 209° (Found : C = 83·4; H = 7·4; N = 9·2. $C_{21}H_{22}N_2$ requires C = 83·4; H = 7·3; N = 9·3 per cent.).

This substance (XXXIV) differs very markedly from (XXXII) in its behaviour with sulphuric acid (50 per cent.), with which it yields a colourless sulphate whereas the sulphate of (XXXII) is scarlet. On the addition of aqueous dichromate to this suspension of the colourless sulphate in dilute sulphuric acid, a deep brownish-yellow partial solution results.

The solution of the substance in much sulphuric acid exhibits only a very slight fluorescence, but this becomes more intense on standing.

Action of Acetic Anhydride.—The substance (XXXIV) shows a curious behaviour on boiling with acetic anhydride and a drop of sulphuric acid. When it (1·5 gms.) was boiled with the anhydride (8 c.c.) alone, it only partly dissolved to a pale yellow solution, but, on addition of a drop of sulphuric acid and continued boiling, a clear deep brownish-red solution soon resulted. After 1 hour's boiling, water was added, the orange solid collected, ground with dilute ammonia, and then boiled with alcohol (50 c.c.) and filtered hot. The residue (0·5 gm.) dissolved in boiling alcohol to an intensely green fluorescent solution and, on cooling, thin yellow plates separated which melted at 181° and consisted of the etheno-derivative (XXXII), as a mixed melting point demonstrated.

It is suggested that this important change is due to the oxidising action of the small quantity of sulphuric acid.

21-*Ethyl*-5 : 10 : 15 : 16 : 17 : 18 : 19 : 20-*octahydroacrindoline* (XXXV).

The ethano-derivative (XXXIV; 6 gms.) was dissolved in warm dilute sulphuric acid (180 c.c. of 60 per cent.) and the deep reddish-brown solution electrolytically reduced in the apparatus described on p. 1798, with a current of 6 amps. for 6 hours at a temperature of

35—45°. The resulting solution was nearly colourless, but an orange substance was deposited on the sides of the beaker, on the cathode, and on the porous cell.

The whole was poured on to ice and water, the solid (*A*) collected, well washed, and dried. The filtrate and washings of (*A*) deposited, on standing, a very sparingly soluble red sulphate which was collected (filtrate *Y*), decomposed by ammonia, and yielded 0·2 gm. of a base which separated from benzene in yellow plates, melted at 181°, and was found to be identical with the etheno-derivative (XXXII). The solid (*A*) consisted essentially of a mixture of two sulphates and, on grinding with dilute ammonia, one was converted into the base and the other remained unchanged.

The light brown solid (4 gms.) obtained after the treatment with dilute ammonia was dried in a vacuum desiccator, and extracted four times with small quantities of boiling light petroleum (b. p. 60—80°) [insoluble residue (*B*)]. The combined extracts were evaporated to a small bulk, and allowed to stand, when stout, reddish-orange prisms (1·2 gms.), m. p. 125°, separated. Recrystallisation raised the melting point to 127° (Found: C = 82·7; H = 7·8; N = 9·0. $C_{21}H_{24}N_2$ requires C = 82·9; H = 7·9; N = 9·2 per cent.). This *ethyloctahydroacrindoline* (XXXV) distilled unchanged and was not affected by treatment with sodium amalgam; reduction with palladium and hydrogen yielded an uncrystallisable syrup which was not further examined. The sulphate is colourless and the solution in dilute sulphuric acid (50 per cent.) yields a deep yellow solution on the addition of aqueous dichromate.

The Acetyl Derivative.—When the base (1 gm.) was heated to boiling with acetic anhydride (6 c.c.) containing a drop of sulphuric acid for an hour, and the excess of anhydride destroyed by water, a brown substance was obtained which was collected, ground with dilute ammonia, dried, and crystallised from light petroleum, from which the acetyl derivative separated in colourless plates, m. p. 173° (Found: C = 80·3; H = 7·4. $C_{21}H_{23}N_2{\cdot}CO{\cdot}CH_3$ requires C = 79·8; H = 7·5 per cent.). On hydrolysis with methyl-alcoholic potassium hydroxide for 3 hours, it yielded ethyloctahydroacrindoline.

21-*Ethyl*-15 : 16 : 17 : 18 : 19 : 20-*hexahydroacrindoline.*

The crude sulphate (*B*, above), not decomposed by dilute ammonia and insoluble in light petroleum, was extracted with boiling alcohol, filtered from insoluble matter (which was largely inorganic), and the solution concentrated and left for several hours, when stout, irregular, brown rhombs separated which melted with decomposition at 230° and consisted of the sulphate of the above base (Found: C =

62·2; H = 6·4. $C_{21}H_{22}N_2,H_2SO_4$ requires C = 63·0; H = 6·0 per cent.). When the alcoholic solution of this sulphate is digested with methyl-alcoholic potassium hydroxide for 4 hours and water added, the solid base is obtained, which separates from light petroleum in well-defined, reddish-brown prisms, m. p. 110—111° (Found: C = 83·5; H = 7·1; N = 9·3. $C_{21}H_{22}N_2$ requires C = 83·4; H = 7·2; N = 9·3 per cent.). This base differs from ethyloctahydroacrindoline in being very readily soluble in light petroleum and is evidently formed by the oxidation of that substance.

21-*Ethyl*-5 : 6 : 7 : 8 : 9 : 10 : 15 : 16 : 17 : 18 : 19 : 20-*dodecahydroacrindoline* (XXXVI).

The filtrate (*Y*, p. 1802) contained a large portion, sometimes the main portion, of the product of the electrolytic reduction of ethanooctahydroacrindoline (XXXIV). It was made alkaline with ammonia, the buff precipitate extracted with ether, dried over anhydrous sodium sulphate, and, after the ether had been removed, the residual gum was distilled under 15 mm., when it passed over as a pale yellow oil which solidified to a brittle resin.

This resinous base was very soluble in cold light petroleum, still more so in alcohol and benzene, and all attempts to obtain it in a crystalline condition were unsuccessful (Found: C = 82·1; H = 9·3. $C_{21}H_{28}N_2$ requires C = 81·8; H = 9·1 per cent.). This resin was then dissolved in dilute hydrochloric acid and fractionally precipitated with very dilute ammonia in three portions, namely, (i) a small initial portion, (ii) the bulk of the material, and (iii) a small final portion. The analysis of (ii) gave C = 81·5; H = 9·3, agreeing still better than the first analysis with the formula $C_{21}H_{28}N_2$. This base gives very readily soluble salts and the deep yellow solution in dilute sulphuric acid (50 per cent.) becomes reddish-brown on the addition of aqueous dichromate.

Action of Acetic Anhydride.—The resinous base (2·5 gms.) was gently boiled with acetic anhydride (10 c.c.) containing a drop of sulphuric acid for an hour, water was then added, when a brown precipitate (*O*) separated which was collected. The filtrate from (*O*) was made alkaline with ammonia, the nearly colourless precipitate collected, and distilled under reduced pressure, when a pale resin was obtained which was evidently the *acetyl* derivative of *ethyldodecahydroacrindoline* (Found: C = 78·5; H = 8·5. $C_{21}H_{27}N_2{\cdot}CO{\cdot}CH_3$ requires C = 78·8; H = 8·6 per cent.).

The solution of this acetyl derivative in dilute hydrochloric acid has a green fluorescence and gives a yellowish-brown precipitate with ferric chloride. The addition of aqueous dichromate to the

solution in dilute sulphuric acid (50 per cent.) produced a reddish-brown coloration with a decided blue tint. On hydrolysis with methyl alcoholic potassium hydroxide, a resinous base was obtained which was again uncrystallisable.

The substance (*O*) also distilled under reduced pressure and solidified to a pale brown resin (Found: C = 74·4; H = 8·3), but no clue was obtained as to its nature.

One of us (W. H. P.) desires to thank the Research Fund of the Royal Society for a grant which has partly defrayed the cost of this investigation. We also wish to thank the British Dyestuffs Corporation for permission to publish some of the experimental work described in this communication. We are indebted to Mr. F. Hall for carrying out the whole of the analyses and to Mr. R. G. Riley for assistance in the preparation of some of the materials.

THE DYSON PERRINS LABORATORY, OXFORD.
THE UNIVERSITY, MANCHESTER. [*Received, May 6th*, 1924.]

CCXXVIII.—*Vinyl Derivatives especially of Carbazole and Tetrahydrocarbazole and their Behaviour with Acids.*

By GEORGE ROGER CLEMO and WILLIAM HENRY PERKIN, jun.

In order to obtain evidence bearing on the constitution of certain synthetical substances supposed to be closely related to strychnine (p. 1766), it became a matter of importance to investigate the characteristics of the 9-vinyl derivatives of substituted carbazoles, and especially to determine their behaviour towards acids. The literature contains very few references to *N*-vinyl derivatives, and this is clearly due to the difficulty of preparing such substances and to their instability. Dimethylvinylamine, $NMe_2 \cdot CH{:}CH_2$ (K. Meyer and Hopff, *Ber.*, 1921, **54**, 2277, 2942), and *N*-methylvinylaniline, $NMePh \cdot CH{:}CH_2$ (von Braun and Kirschbaum, *Ber.*, 1919, **52**, 2264), polymerise more or less readily and are converted by warm dilute mineral acids into acetaldehyde and dimethylamine and methylaniline, respectively.

In these cases, the ready decomposition by acids may, in part, be due to the strongly basic nature of dimethylamine or methylaniline and, in order to test this view, it seemed desirable to prepare acyl derivatives of vinylaniline, hitherto apparently unknown, and to find out whether such substances would decompose, in contact with acids, into acetaldehyde and acyl derivatives devoid of basic pro-

perties. We have succeeded in preparing substances of this type by the following series of reactions.

The sodium derivative of toluene-*p*-sulphonanilide reacts in aqueous solution with β-chloroethyl toluene-*p*-sulphonate (J., 1922, 121, 644), yielding *toluene*-p-*sulphon*-β-*chloroethylanilide* (I), and this, on boiling with methyl alcoholic potash, is converted into *toluene*-p-*sulphonvinylanilide* (II).

$$PhNNa{\cdot}SO_2{\cdot}C_6H_4Me + C_6H_4Me{\cdot}SO_3{\cdot}CH_2{\cdot}CH_2Cl \longrightarrow$$
$$PhN(CH_2{\cdot}CH_2Cl){\cdot}SO_2{\cdot}C_6H_4Me\ (I.) \longrightarrow PhN(CH{:}CH_2){\cdot}SO_2{\cdot}C_6H_4Me\ (II.)$$

The chlorine atom in toluenesulphon-β-chloroethylanilide (I) is sufficiently labile to react with amines, amino-derivatives, and with phenolic substances, and the toluene-*p*-sulphonyl derivatives thus obtained yield, on hydrolysis, unsymmetrically substituted ethylenediamines or derivatives of β-phenoxyethylaniline.

$$(I.) \longrightarrow PhN(CH_2{\cdot}CH_2{\cdot}OPh){\cdot}SO_2{\cdot}C_6H_4Me \longrightarrow PhNH{\cdot}CH_2{\cdot}CH_2{\cdot}OPh.$$
$$\downarrow$$
$$PhN(CH_2{\cdot}CH_2{\cdot}NEt_2){\cdot}SO_2{\cdot}C_6H_4Me \longrightarrow PhNH{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_2.$$

On the other hand, although the chlorine atom can be replaced by iodine, we have not succeeded in preparing the corresponding cyanide.

When the substance (I) is hydrolysed with a mixture of acetic and hydrochloric acids, it is readily converted into β-chloroethylaniline hydrochloride. On decomposing this hydrochloride by alkali, the base separates at first as an oil, but this rapidly changes to a colourless, solid base which is free from chlorine and the constitution of which has not been determined.

It is curious that diphenylpiperazine is not produced in these circumstances. β-Chloroethylaniline reacts with benzoyl chloride; the crystalline substance obtained by shaking the product with caustic soda solution is *benzo*-β-*hydroxyethylanilide*,

$$C_6H_5{\cdot}N(CO{\cdot}C_6H_5){\cdot}CH_2{\cdot}CH_2{\cdot}OH,$$

benzoylation and replacement of the chlorine atom by hydroxyl having taken place simultaneously.

β-Chloroethylaniline readily yields an oily *nitrosoamine*, and, on treatment with alcoholic hydrochloric acid, this undergoes molecular change and yields a hydrochloride which crystallises in yellow prisms; the base itself, which doubtless has the formula $NO{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}CH_2Cl$, separates from benzene in dark green plates melting at 90°. It is strange that there is apparently only one reference to β-chloroethylaniline in the literature. Nemirowsky (*J. pr. Chem.*, 1885, [ii], **31**, 175), who obtained the hydrochloride by

heating carbanilchloroethyl ester with hydrochloric acid at 170°, states that it melts at 158° and that the base itself is unstable. The isomeric *o*- and *p*-β-chloroethylanilines, $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2Cl$, have been prepared by von Braun (*Ber.*, 1912, **45**, 1277), and it is remarkable that, in these cases also, the free bases are unstable and change, on warming, into amorphous insoluble substances of unknown composition (compare also Gabriel and Colman, *Ber.*, 1914, **47**, 1866).

Toluene-p-*sulphonvinylanilide* (II) readily takes up 2 atoms of bromine with the formation of an unstable substance which is evidently *toluene*-p-*sulphon*-α*β*-*dibromoethylanilide*,

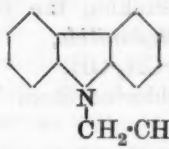
$$C_6H_5 \cdot N(CHBr \cdot CH_2Br) \cdot SO_2 \cdot C_6H_4Me,$$

and this is decomposed by aqueous caustic soda with the separation of toluene-*p*-sulphonanilide. If, however, this dibromo-derivative is stirred with warm methyl alcoholic potash, a stable, crystalline substance is produced which is evidently *toluene*-p-*sulphon*-β-*bromo*-α-*methoxyethylanilide*, $C_6H_5 \cdot N[CH(OMe) \cdot CH_2Br] \cdot SO_2 \cdot C_6H_4Me$.

Toluene-*p*-sulphonvinylanilide (II) is very readily acted on by warm dilute sulphuric acid, and the oil which is first produced is soon decomposed with elimination of acetaldehyde and formation of toluene-*p*-sulphonanilide. Clearly, then, the basicity of the product of decomposition has nothing to do with the elimination of the vinyl group as acetaldehyde.

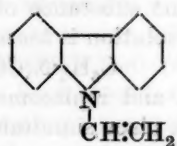
We next directed our attention to the preparation and examination of the vinyl derivatives of carbazole and tetrahydrocarbazole with the view of determining their stability towards acids. In the first place, 9-β-*chloroethylcarbazole* (III) was prepared from carbazole by treatment with β-chloroethyl toluene-*p*-sulphonate in acetone solution in presence of caustic soda (compare Stevens and Tucker, J., 1923, **123**, 2141). When this substance is digested with methyl-alcoholic potash, it readily yields 9-*vinylcarbazole* (IV).

(III.)



$CH_2 \cdot CH_2Cl$

(IV.)



$CH{:}CH_2$

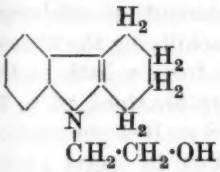
The investigation of the action of acids on 9-vinylcarbazole presented unexpected difficulties. When this substance was warmed with a mixture of acetic and hydrochloric acids, it immediately changed into a solid from which no carbazole or aldehyde could be obtained, and in this respect the substance behaved quite differently from the simpler vinylamines discussed in the earlier part of this communication. After a long series of experiments, it occurred to us that

the acetaldehyde, which should be produced if the decomposition proceeded normally, might interact with the carbazole to yield the curious solid of unknown composition which is the actual product. That this is evidently the case is proved by the fact that if a small quantity of hydrazine hydrate is added prior to the treatment with hydrochloric acid a practically quantitative yield of carbazole is obtained. It is clear, therefore, that 9-vinylcarbazole decomposes normally on treatment with acids into carbazole and acetaldehyde.

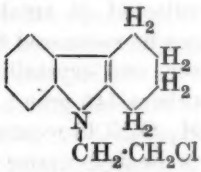
Of still greater importance, from the point of view of the synthetical experiments in the strychnine series described in the preceding paper, were the preparation and investigation of 9-vinyltetrahydrocarbazole. The former proved to be a difficult problem, for β-chloroethyltetrahydrocarbazole could not be prepared by introducing the group $\cdot CH_2 \cdot CH_2Cl$ directly and an indirect method had to be worked out. In the first series of experiments, β-hydroxyethylaniline was converted into the nitroso-derivative,

$$C_6H_5 \cdot N(NO) \cdot CH_2 \cdot CH_2 \cdot OH,$$

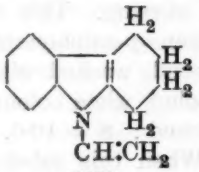
which was reduced with zinc dust in presence of *cyclo*hexanone, when condensation took place readily with the formation of 9-β-hydroxyethyltetrahydrocarbazole (V). This could not be converted into 9-β-chloroethyltetrahydrocarbazole (VI), and therefore preparation of 9-vinyltetrahydrocarbazole (VII) from the latter by means of alcoholic potash was impossible.



(V.)



(VI.)



(VII.)

When (V) was heated in a sealed tube with alcoholic hydrochloric acid at 160°, it was recovered unchanged; thionyl chloride reacted vigorously with the formation of a substance from which nothing definite could be isolated; and phosphorus trichloride yielded an acid containing phosphorus, from which (V) was regained on boiling with alcoholic potash. Lastly, when (V) was distilled under reduced pressure with fused potash, traces of a substance were obtained which appeared to be the impure vinyl derivative.

Ultimately, the chloro-derivative (VI) was obtained in quantity by the following direct process. β-Chloroethylaniline (p. 1805) was converted into the nitroso-derivative, $C_6H_5 \cdot N(NO) \cdot CH_2 \cdot CH_2Cl$, and this reduced in acetic acid solution, in presence of *cyclo*hexanone, with zinc dust, when the chlorine atom remained unaffected; on addition of water, 9-β-chloroethyltetrahydrocarbazole (VI) separated.

On digestion with methyl alcoholic potash, the elimination of hydrogen chloride proceeded smoothly and 9-*vinyltetrahydrocarbazole* (VII) was obtained. This substance, like 9-vinylcarbazole, behaves in a curious manner with mineral acids, yielding a solid substance from which no tetrahydrocarbazole can be isolated. By employing the device (p. 1807) of adding hydrazine hydrate before the treatment with acid, the decomposition proceeds normally, and the substance which separates in almost quantitative yield is tetrahydrocarbazole. Clearly, therefore, 9-vinyltetrahydrocarbazole also is decomposed by mineral acids into acetaldehyde and tetrahydrocarbazole.

The results obtained during the course of this and previous investigations indicate that *N*-vinyl derivatives either of strong bases, like dimethylamine or methylaniline, or of weak bases, like carbazole or tetrahydrocarbazole, are all decomposed by acids with elimination of acetaldehyde and formation of the bases of which they are the derivatives.

EXPERIMENTAL.

Toluene-p-*sulphon*-β-*chloroethylanilide* (I).—A solution of toluene-*p*-sulphonanilide (49·5 gms.) in warm caustic soda (8 gms.) and water (80 c.c.) was mixed with β-chloroethyl toluene-*p*-sulphonate (47 gms.) and heated with stirring in a water-bath for 6½ hours, caustic soda (25 c.c. of 8 per cent.) being added after 6 hours. The reaction mixture, poured into ice-water, yielded a heavy gum, which solidified on stirring. This was collected (a small amount of unchanged toluene-*p*-sulphonanilide can be recovered by acidifying the filtrate), ground, washed with water, and crystallised from a little methyl alcohol, when colourless prisms (46 gms.) were obtained, m. p. 76° (Found: S = 10·6. $C_{15}H_{16}O_2NClS$ requires S = 10·4 per cent.).

When this substance is heated under reflux in amyl alcohol solution with potassium iodide, it is converted into its iodo-analogue, prisms, m. p. 81—82°.

Toluene-p-*sulphonvinylanilide* (II).—The β-chloroethyl compound (I) (8 gms.) was heated under reflux for 5 hours with methyl-alcoholic potash (60 c.c. of 10 per cent.), the bulk of the alcohol was then distilled under reduced pressure, and water added. The resulting colourless solid, well washed with water and dried (yield 6·5 gms.; m. p. 90°) separated from ligroin (b. p. 100—120°) in long, colourless prisms, m. p. 96—97° (Found: C = 66·2; H = 5·7; N = 5·1. $C_{15}H_{15}O_2NS$ requires C = 65·9; H = 5·5; N = 5·1 per cent.).

When this substance was stirred and heated with sulphuric acid (50 per cent.) in the water-bath, a faintly purple oil resulted, which soon became colourless, and acetaldehyde was detected by its odour. The colourless oil, which solidified on cooling, was toluene-*p*-sulphonanilide.

Action of bromine. A solution of the vinyl derivative (2·7 gms.) in carbon tetrachloride (10 c.c.) was treated in the cold with bromine (0·5 c.c.) in carbon tetrachloride (5 c.c.). The bromine was absorbed at once with slight evolution of heat and, on cooling and scratching, a colourless solid crystallised. This was quickly collected, washed with ligroin, and stirred for 10 minutes at 40—45° with methyl-alcoholic potash (10 c.c. of 20 per cent.). Water was added, the solid collected, washed with water, dried (2·3 gms.; m. p. 73—75°), and crystallised from methyl alcohol, when flat, colourless prisms separated, m. p. 78—79° (Found: C = 49·9; H = 4·9; N = 3·5. $C_6H_5{\cdot}N[CH(OMe){\cdot}CH_2Br]{\cdot}SO_2{\cdot}C_6H_4Me$ requires C = 49·9; H = 4·8; N = 3·6 per cent.).

This compound can be heated for 4 hours in the water-bath with dilute caustic soda and recovered unchanged. It is also unchanged by refluxing with aniline in amyl alcohol for 2 hours. If the unstable dibromo-compound is heated with caustic soda solution instead of methyl-alcoholic potash, it is converted, in a few minutes, into toluene-*p*-sulphonanilide.

Action of diethylamine. The chloroethyl derivative (I) (27·9 gms.) was heated for 9 hours in a sealed tube at 160° with alcoholic diethylamine (2 equivs.). The alcohol was then removed, and the product hydrolysed by gently heating under reflux for 3 hours with acetic acid (40 c.c.) and hydrochloric acid (100 c.c.). The bulk of the acids was then removed by heating in the water-bath under reduced pressure, the residue made alkaline, and the liberated base extracted with benzene and fractionated, when 14·5 gms. of a colourless, almost odourless, strongly basic oil passed over at 163°/17 mm. (Found: N = 14·3. $C_{12}H_{20}N_2$ requires N = 14·6 per cent.). This substance is β-*diethylaminoethylaniline* (p. 1805).

Action of o-*chloroaniline.* The chloroethyl derivative (I) (9·3 gms.) was refluxed for 6 hours with o-*chloroaniline* (10 gms.), potassium carbonate (2·1 gms.), and a trace of copper powder. The mixture was then steam-distilled and the residual sulphonyl derivative crystallised from alcohol, from which it separated in colourless plates, m. p. 110° (Found: N = 6·9. $C_{21}H_{21}O_2N_2ClS$ requires N = 7·00 per cent.).

This sulphonyl derivative was hydrolysed with acetic and hydrochloric acids exactly as described above and the β-o-*chlorophenylaminoethylaniline* distilled, when it passed over as an oil at 238—242°/20 mm. and up to the present has not been obtained in the solid form (Found: N = 11·3. $C_{14}H_{15}N_2Cl$ requires N = 11·4 per cent.). Its crystalline *hydrochloride* has m. p. 185°.

Hydrolysis of Toluene-p-*sulphon*-β-*chloroethylanilide.*—A mixture of the anilide (I) (28 gms.) with acetic acid (135 c.c.) and hydro-

chloric acid (135 c.c.) was gently heated under reflux for 4 hours and then poured on ice. The slightly turbid solution was kept for 1 hour, a trace of unhydrolysed material which crystallised out was filtered off, and the clear acid solution, containing the β-chloroethylaniline, divided into three equal parts.

One part, well cooled, was shaken with benzene and made alkaline. The benzene layer, containing the β-chloroethylaniline, was quickly separated, and dry hydrogen chloride passed, when *β-chloroethylaniline hydrochloride* crystallised in thin, colourless prisms, m. p. 156—158°. When this was decomposed by warm alkali, the free base separated as an oil, which quickly polymerised, especially on warming, to a colourless, weakly basic solid, free from chlorine, the constitution of which is unknown.

A second part of the acid filtrate was cooled, mixed with benzene (60 c.c.) containing benzoyl chloride (9 c.c.), made alkaline, and shaken at intervals for an hour; the aqueous layer was then run off, and the benzene layer twice washed with water and steam-distilled. The residual heavy oil solidified on cooling (yield 6—7 gms.) and was crystallised twice from ligroin, when colourless, slender prisms of *benzo-β-hydroxyethylanilide* were obtained, m. p. 78° [Found: N = 5·5. $C_6H_5{\cdot}N(CO{\cdot}C_6H_5){\cdot}CH_2{\cdot}CH_2{\cdot}OH$ requires N = 5·8 per cent.].

Further benzoylation of this substance yielded the dibenzoyl derivative, m. p. 92° (*Ber.*, 1904, **37**, 3942).

The remaining part of the acid filtrate was kept cold, stirred, and an aqueous solution of sodium nitrite (2·5 gms. $NaNO_2$ in 10 c.c.) added. The nitroso-derivative, which separated as a heavy oil on standing, was dissolved in ether and treated at the ordinary temperature with alcoholic hydrochloric acid (20 c.c.), when about 3 gms. of yellow prisms of the hydrochloride of *p*-nitroso-β-chloroethylaniline, $NO{\cdot}C_6H_4{\cdot}NH{\cdot}C_2H_4Cl,HCl$, were obtained, m. p. 182° (decomp.). When this was treated with sodium carbonate, and the free nitroso-compound crystallised from benzene–ligroin, brilliant dark green plates with a steel blue reflex were obtained which melted at 90° and decomposed explosively at 120° (Found: C = 52·0; H = 4·9; N = 15·2; Cl = 19·2. $NO{\cdot}C_6H_4{\cdot}NH{\cdot}C_2H_4Cl$ requires C = 52·3; H = 5·1; N = 15·1; Cl = 19·1 per cent.).

9-β-*Chloroethylcarbazole* (III).—Carbazole (21 gms.) was dissolved in acetone (150 c.c.), β-chloroethyl toluene-*p*-sulphonate (50 gms.) and caustic soda (21 gms.) in water (15 c.c.) were added, and the mixture was stirred for 2½ hours in a water-bath at 50—60°. A further quantity of the ester (10 gms.) together with caustic soda (4·2 gms.) in water (3 c.c.) was then added and the heating at 50—60° and stirring were continued for 2½ hours longer. The bulk of

the acetone was then distilled off, ice-water added, and the buttery solid collected, well pressed on porous porcelain, and extracted with ligroin, when 7·6 gms. of carbazole remained undissolved. The ligroin extract deposited, on standing, a soft, crystalline mass, which was collected and crystallised from alcohol, when colourless prisms (11·2 gms.) separated, m. p. 125—126°. This material was finally crystallised from ligroin (b. p. 80—100°), when the long, glistening prisms melted at 130—131° (Found: C = 73·5; H = 5·1. $C_{14}H_{12}NCl$ requires C = 73·2; H = 5·2 per cent.).

9-β-*Chloroethylcarbazole* dissolves in concentrated sulphuric acid to a pale yellow solution, which changes to intense bluish-green on the addition of a trace of solid potassium dichromate, and to a deep grass green on the addition of nitric acid.

9-*Vinylcarbazole* (IV).—9-β-Chloroethylcarbazole (2 gms.) was dissolved in alcohol (40 c.c.), methyl-alcoholic potash (30 c.c. of 25 per cent.) added, and the mixture heated under reflux for 5 hours. The bulk of the alcohol was then distilled off, the residue poured on ice, and, after standing for 30 minutes, the colourless precipitate was collected and crystallised from alcohol, from which 9-*vinylcarbazole* separated in thin plates, m. p. 66° (Found: C = 87·4; H = 5·6. $C_{14}H_{11}N$ requires C = 87·0; H = 5·7 per cent.).

Action of acids. A solution of 9-vinylcarbazole (0·4 gm.) in alcohol (4 c.c.) was gently boiled for about a minute with ethyl-alcoholic hydrochloric acid (4 c.c.), when a colourless solid separated. Ice and an excess of ammonia were introduced and the colourless solid was collected and extracted with a little boiling alcohol to remove a small amount of insoluble matter. The alcohol was removed; the residue, on dry distillation, underwent considerable decomposition and a small quantity of carbazole sublimed.

In another experiment, 9-vinylcarbazole (0·4 gm.) was dissolved in alcohol (4 c.c.), hydrazine hydrate (0·5 c.c.) added, and then to the warm solution, ethyl-alcoholic hydrochloric acid (4 c.c.) was slowly run in, when a colourless precipitate immediately formed. The mixture was boiled for about 15 seconds, ice and an excess of ammonia were added, and the solid was collected and dissolved in a small volume of alcohol, when, on cooling, thin, colourless plates of carbazole (0·3 gm.), m. p. 236°, separated. The yield of carbazole produced under these conditions was therefore almost that theoretically possible.

9-β-*Hydroxyethyltetrahydrocarbazole* (V).—A solution of β-hydroxyethylaniline (13·7 gms.) in concentrated hydrochloric acid (15 c.c.) was mixed with ice and stirred while aqueous sodium nitrite (7·2 gms.) was run in; a heavy oil separated. The acid layer was

extracted with ether, the heavy oil and the ether extract were dissolved in acetic acid (30 c.c.) and mixed with *cyclo*hexanone (15 c.c.), and then zinc dust (20 gms. of 90 per cent.) was added, with stirring, during 30 minutes. Considerable heat was developed, but the temperature was maintained at 25—35° during the addition of the zinc dust and then raised to 40—45° for about 10 minutes. The whole was filtered, the zinc residues were stirred with a little acetic acid, and the combined acid filtrates were heated at 60° for about 10 minutes and poured on to ice, when a heavy, viscid precipitate separated, which was extracted with ether. After removal of the ether, the oil (10 gms.) passed over between 230—235°/14 mm. This was dissolved in ligroin containing a little benzene, and, on standing, colourless, ill-defined, waxy prisms gradually separated, m. p. 69—70° (Found: C = 78·5; H = 7·9. $C_{14}H_{17}ON$ requires C = 78·1; H = 7·9 per cent.).

When this colourless substance is kept for 24 hours, it becomes light lemon-coloured.

9-β-*Chloroethyltetrahydrocarbazole* (VI).—Toluenesulphon-β-chloroethylanilide (I) (28 gms.) was hydrolysed as described on pp. 1809, 1810, and the cold acid filtrate stirred while an aqueous solution of sodium nitrite (7·5 gms.) in water (30 c.c.) was run in. The heavy oily nitroso-derivative (11 gms.) was separated, and the aqueous layer shaken with a little ether, when the remainder of the nitroso-compound, which had been in suspension, settled out as a heavy layer. The combined portions of the nitroso-derivative were treated as in the preceding experiment (acetic acid 37 c.c.; *cyclo*hexanone 15 c.c.; 90 per cent. zinc dust 18 gms.; temperature, initial 25—30°, final 35°). The combined acid filtrates were heated for 5 minutes at 65°, the resulting reddish-brown solution poured into water, and the mixture steam-distilled until about 300 c.c. of distillate had passed over. The residue was poured on to ice, when a pale brown gum settled out, which, on stirring with a little methyl alcohol, gradually set to a light brown solid (6 gms.). The solution of this in methyl alcohol deposited a gum at first, but on standing, stout, colourless prisms separated (4 gms.) * and, on concentrating the alcoholic solution, a further quantity (1 gm.) was obtained.

* In some experiments, this substance contained a small amount of a by-product, which was separated from VI by means of its sparing solubility in ligroin. This substance crystallised from ligroin (b. p. 80—100°) in faintly brown, thin, flat prisms, m. p. 141° (Found: C = 59·6; H = 5·8; N = 15·6; Cl = 19·4. $C_2H_4Cl{\cdot}NPh{\cdot}NH{\cdot}NH{\cdot}NPh{\cdot}C_2H_4Cl$ requires C = 59·1; H = 5·9; N = 15·3; Cl = 19·4 per cent.). The substance dissolves in sulphuric acid to a deep brown solution, the colour of which is changed to a beautiful purplish-blue and to an intense bluish-red by the addition of potassium dichromate and nitric acid, respectively; the latter solution

9-β-*Chloroethyltetrahydrocarbazole* separates from methyl alcohol in well-defined, colourless, rhombic prisms which slowly transform into elongated prisms, melting at 56—57° (Found: C = 71·9; H = 6·9; N = 5·9. $C_{14}H_{16}NCl$ requires C = 72·1; H = 6·9; N = 6·0 per cent.). In marked contrast to (III), the almost colourless sulphuric acid solution of (VI) gives no coloration with nitric acid and only a dull brown colour with potassium dichromate.

9-*Vinyltetrahydrocarbazole* (VII).—To a solution of 9-β-chloroethyltetrahydrocarbazole (VI) (5 gms.) in methyl alcohol (50 c.c.), methyl-alcoholic potash (50 c.c. of 25 per cent.) was added, and the mixture gently heated under reflux for 5 hours. The bulk of the alcohol was then removed, water added, the precipitated colourless, heavy oil extracted with ether, and the extract dried and fractionated, when a colourless oil (3·8 gms.) passed over at 210°/24 mm. (Found: C = 84·9; H = 7·7. $C_{14}H_{15}N$ requires C = 85·3; H = 7·6 per cent.).

The action of acids. Expt. I. The substance (0·5 gm.) was stirred with sulphuric acid (3 c.c. of 50 per cent.), when a colourless, granular solid was quickly produced. This was collected, ground with ammonia, dried, and distilled under reduced pressure, when a small quantity of distillate was obtained which, however, did not appear to contain any tetrahydrocarbazole.

Expt. II. The above experiment was repeated, but a little hydrazine hydrate was added to the sulphuric acid prior to its addition to the oil. In this case, a considerable amount of a distillate was obtained which solidified and, after crystallisation from ligroin, melted at 116° and consisted of tetrahydrocarbazole.

Expt. III. The substance (0·5 gm.) was dissolved in alcohol (4 c.c.) and alcoholic hydrochloric acid (4 c.c.) added, when a deep yellow solution resulted which, on boiling for 15 seconds, changed to a dull green. Ice and excess of ammonia were added, and the colourless solid was collected, dried, and heated in a hard glass tube under reduced pressure. There was much decomposition, and a small amount of distillate was obtained which was almost insoluble in ligroin (b. p. 80—100°) and from which no tetrahydrocarbazole could be isolated.

Expt. IV. This was a repetition of Expt. III, but hydrazine hydrate was added prior to the alcoholic hydrochloric acid. A considerable amount of a solid distillate was obtained which was

---

quickly becomes colourless. When the substance is treated with methyl-alcoholic potash, a product free from chlorine is obtained which crystallises from ligroin in thin, yellow plates, m. p. 166—167°, but the amount of material was insufficient for further investigation.

completely soluble in boiling ligroin and, on cooling, tetrahydrocarbazole separated in quantity.

We are again indebted to the British Dyestuffs Corporation for permission to publish these results.

THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, May 6th*, 1924.]

CCXXIX.—*Studies in the Configuration of αα′-Dibromodibasic Acids. Part III. The αα′-Dibromosuccinic Acids.*

By HARRY RAYMOND ING and WILLIAM HENRY PERKIN, jun.

IN Part I of this series (J., 1921, **119**, 1392), a method was suggested for the determination of the configuration of αα′-dibromo-dibasic acids by the condensation of their esters with the sodium derivative of malonic ester to form cyclic products, the configuration of which might then be readily ascertained by resolution or in other ways. In the present paper, an account is given of the condensations of the αα′-dibromosuccinic esters with the sodium derivatives of malonic, cyanoacetic, benzoylacetic, and acetoacetic esters.

There are two αα′-dibromosuccinic acids: one melts at 167° and was resolved into its optical enantiomorphs by McKenzie (J., 1912, **101**, 1196) and is consequently the racemic or *dl*-acid; the other acid, which sublimes above 280°, must therefore be the *meso*-isomeride.

The methyl and ethyl esters of *dl*-dibromosuccinic acid were described by Pictet (*Ber.*, 1880, **13**, 1671) as oils which could not be distilled without decomposition. Michael (*Ber.*, 1901, **34**, 4220) claimed to have obtained the ethyl ester from dibromosuccinic anhydride, but he described it as decomposing on distillation even under reduced pressure. We have obtained both the methyl and the ethyl ester by the addition of dry bromine to a dry ethereal solution of the corresponding maleic ester. Methyl *dl*-dibromosuccinate is a solid melting at 43°, and the ethyl ester is an oil distilling unchanged at 137—138°/11 mm. Both the methyl and the ethyl ester can also be made by the direct esterification of the *dl*-acid or from its silver salt.

The methyl and ethyl esters of *meso*-dibromosuccinic acid were obtained by the addition of bromine to the corresponding fumaric esters, as described by Anschütz (*Ber.*, 1879, **12**, 2281); they are solids, melting at 65° and 58°, respectively. The dibromination

of succinyl chloride does not appear to yield structural isomerides as R. Meyer and Marx (*Ber.*, 1908, **41**, 2466) suggest; the product is clearly a mixture of the chlorides of the *meso*- and *dl*-dibromosuccinic acids, since on treatment with alcohol, a mixture of the *meso*- and the *dl*-ester is obtained. The condensations described in the present communication have been divided, for the sake of convenience, into sections A, B, C, and D.

Section A.—The condensation of ethyl *meso*-dibromosuccinate with ethyl sodiomalonate was first investigated by Perkin (J., 1885, **47**, 823). The main product was a high-boiling oil which yielded on hydrolysis a tetrabasic acid, $C_7H_6O_8$, melting at 95—100° with decomposition; this acid was considered to be *cis-cyclo*propane-1 : 2 : 3-tetracarboxylic acid. When this acid was heated above its melting point, it lost carbon dioxide and gave a tribasic acid, $C_6H_6O_6$, melting at 150—153°, which was assumed to be *cis-cyclo*propane-1 : 2 : 3-tricarboxylic acid. Later Buchner (*Annalen*, 1895, **24**, 225) carried out the same condensation, using, however, the methyl esters. He obtained two solid products, namely, methyl ethanetetracarboxylate, methyl *cyclo*propanetetracarboxylate, and an oil. The *cyclo*propane ester (m. p. 85°) yielded, on hydrolysis, *trans-cyclo*propane-1 : 2 : 2 : 3-tetracarboxylic acid, m. p. 198°, and this acid, by loss of carbon dioxide, gave *trans-cyclo*propane-1 : 2 : 3-tricarboxylic acid, m. p. 220°. The oil yielded on hydrolysis an acid which Buchner assumed to be identical with the tetrabasic acid obtained by Perkin, since it decomposed with loss of carbon dioxide at 100°.

In the present investigation, both the methyl and the ethyl esters of the isomeric dibromosuccinic acids have been used in the condensations with the sodium derivative of the corresponding malonic ester. In each case the dibromo-ester (1 mol.) was added to an ice-cold suspension of the sodiomalonic ester (2 mols.) in absolute alcohol.

The *dl*-dibromosuccinic esters were found to give an 80—90 per cent. yield of the corresponding *cyclo*propane ester (equation 1).

$$(1)\quad \begin{matrix}CO_2R\cdot CHBr\\ CO_2R\cdot CHBr\end{matrix} + 2NaCH\cdot(CO_2R)_2 \longrightarrow \begin{matrix}CO_2R\cdot CH\\ CO_2R\cdot CH\end{matrix}\!\!>C(CO_2R)_2 + CH_2(CO_2R)_2 + 2NaBr.$$

Both esters yield, on hydrolysis, *cyclo*propane-1 : 2 : 2 : 3-tetracarboxylic acid, which loses carbon dioxide above 198° (m. p. of the anhydrous acid) to give *cyclo*propane-1 : 2 : 3-tricarboxylic acid.

The *meso*-dibromosuccinic esters on treatment with the sodium

derivative of the corresponding malonic ester were found to yield a mixture of several substances. In the case of the methyl esters, the following products were isolated from the reaction mixture: methyl fumarate, methyl ethanetetracarboxylate,

$$(CO_2Me)_2CH{\cdot}CH(CO_2Me)_2,$$

methyl *cyclo*propanetetracarboxylate, and an oil which was shown to be methyl α-carbomethoxytricarballylate,

$$CO_2Me{\cdot}CH_2{\cdot}CH(CO_2Me){\cdot}CH(CO_2Me)_2,$$

by its hydrolysis to tricarballylic acid. This *meso*-condensation seems to proceed in two directions simultaneously and to approximately the same extent; in the one case, it yields the *cyclo*propane ester and methyl malonate (equation 1), and in the other, methyl fumarate and methyl ethanetetracarboxylate (equation 2).

$$(2)\quad \begin{matrix} CO_2Me{\cdot}CHBr \\ CO_2Me{\cdot}CHBr \end{matrix} + 2CHNa(CO_2Me)_2 \longrightarrow \begin{matrix} CO_2Me{\cdot}CH \\ CO_2Me{\cdot}CH \end{matrix} + \begin{matrix} CH(CO_2Me)_2 \\ CH(CO_2Me)_2 \end{matrix} + 2NaBr.$$

Finally, in presence of sodium methoxide, methyl fumarate adds on methyl malonate to give methyl α-carbomethoxytricarballylate.

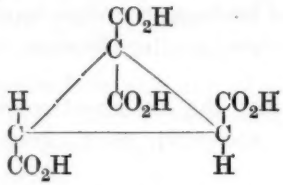
It is noteworthy that the same *cyclo*propane ester is formed from both the *dl*- and the *meso*-dibromosuccinic esters, though in much smaller amount from the *meso*-ester. The reason for this formation in the latter case is discussed later (Section B). It seems, therefore, that the two acids obtained by Perkin (*loc. cit.*) were not pure *cyclo*propane acids; the tetrabasic acid melting at 95—100° was probably a mixture of α-carboxytricarballylic acid and *cyclo*propanetetracarboxylic acid, whilst the tribasic acid melting at 150—153° was similarly a mixture of tricarballylic acid and *cyclo*propanetricarboxylic acid. Consequently, only one *cyclo*propane-1 : 2 : 2 : 3-tetracarboxylic acid has so far been isolated, namely, that obtained by Buchner which melts at 198°. Two *cyclo*propane acids of this constitution are, however, theoretically possible, namely (I) and (II), and of these, the *trans*-acid (I) should be capable of resolution into optically active isomerides. Similarly, only one *cyclo*propane-1 : 2 : 3-tricarboxylic acid has been definitely isolated, namely, that melting at 220°, whereas two, (III) and (IV), are theoretically possible. Buchner assigned the *trans*-configuration (I) to the tetracarboxylic acid melting at 198°, on the basis of its high melting point; and for the same reason he gave the tricarboxylic acid, m. p. 220°, the *trans*-configuration (III).

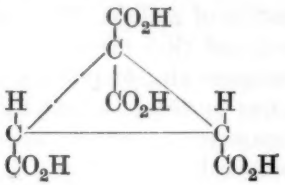
In order to establish the configuration of the *cyclo*propane-1 : 2 : 2 : 3-tetracarboxylic acid of melting point 198°, resolution

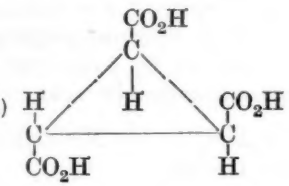
experiments were instituted. The fractional crystallisation of the brucine salt of the acid yielded finally a salt,

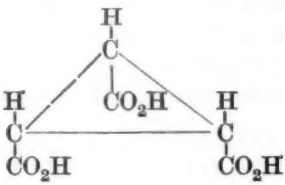
$$C_7H_6O_8,4C_{23}H_{26}O_4N_2,2H_2O,$$

of constant rotation, from which pure *d-cyclo*propane-1 : 2 : 2 : 3-tetracarboxylic acid was isolated; it melted at 195°, and in water had $[\alpha]_D^{18°} = +106{\cdot}5°$. Consequently, the *cyclo*propanetetracarboxylic acid of melting point 198° must have the configuration (I). An examination of the models shows that neither of the tribasic acids, (III) and (IV), can exist in optically active forms, and also that the acid (II), by loss of carbon dioxide, can give rise to either or both of the acids (III) and (IV), whereas the *dl*-acid (I) can yield directly only the *trans*-acid (III) in these circumstances. The *cyclo*propanetricarboxylic acid of Buchner, which melts at 220° and is produced by loss of carbon dioxide from *dl-cyclo*propanetetracarboxylic acid, appears, therefore, to be represented by formula (III).









*cyclo*Propane-1 : 2 : 2 : 3-tetracarboxylic acid is remarkable for its stability, as it does not decompose with loss of carbon dioxide until 200°, and it is unaffected by boiling with concentrated hydrochloric acid. This stability may be attributed to the relatively large angle between the two carboxyl groups attached to the same carbon atom, a result due to the smallness of the internal angle (60°) of the *cyclo*propane ring. This property is particularly interesting in view of the results recorded in Part II of this series, where it was shown that *cyclo*pentane-1 : 2 : 2 : 3-tetracarboxylic acid could not even be isolated owing to the ease with which it loses carbon dioxide. It may be assumed that this difference in behaviour is the result of the proximity of the carboxyl groups due to the larger angle (108°) of the *cyclo*pentane ring. The fact that *dl-cyclo*propanetetracarboxylic acid is produced smoothly from the acid known on other grounds to be *dl*-dibromosuccinic acid is in favour of the

view, put forward in Parts I and II of this series of researches, that condensations of this kind, followed by the resolution of the resulting acid, can be taken as evidence of the configuration of the dibromo-acid employed in the synthesis.

Section B.—The formation of *dl-cyclo*propanetetracarboxylic ester from *meso*dibromosuccinic ester (p. 1816) is probably due to the intermediate stage of bromomaleic ester, which, according to Buchner (*Annalen*, 1895, **284**, 223), condenses with sodiomalonic ester to yield *cyclo*propanetetracarboxylic ester (equation 3).

$$(3)\quad \begin{matrix}CO_2R\cdot CH\\ CO_2R\cdot CBr\end{matrix}\!\!\!

of formation, may be either ethyl 1-benzoyl*cyclo*propane-1 : 2 : 3-tricarboxylate (VII) or ethyl 5-phenyl-2 : 3-dihydrofuran-2 : 3 : 4-tricarboxylate (VIII).

(VII.) $\begin{matrix} CO_2Et\cdot CH \\ CO_2Et\cdot CH \end{matrix}\!>\!C\!<\!\begin{matrix} COPh \\ CO_2Et \end{matrix}$ $\qquad$ $\begin{matrix} CO_2Et\cdot CH\!-\!C\cdot CO_2Et \\ CO_2Et\cdot CH \quad\; CPh \\ \qquad\quad \diagdown\; \diagup \\ \qquad\quad\;\; O \end{matrix}$ (VIII.)

Hydrolysis of the ester $C_{19}H_{22}O_7$ with cold methyl-alcoholic potassium hydroxide led to the formation of a potassium salt from which a tribasic acid, $C_{13}H_{12}O_8$, was isolated. The *cyclo*propane ester (VII) could only yield a tribasic acid of composition $C_{13}H_{10}O_7$ (IX), but the ester (VIII), by the rupture of the dihydrofuran ring, could yield a tribasic acid $C_{13}H_{12}O_8$, namely, α-hydroxy-γ-benzoyltricarballylic acid (X); consequently the acid actually obtained by us probably has this constitution. It melts at 142—143° with

(IX.) $\begin{matrix} CO_2H\cdot CH \\ CO_2H\cdot CH \end{matrix}\!>\!C\!<\!\begin{matrix} COPh \\ CO_2H \end{matrix}$ $\qquad$ $\begin{matrix} CO_2H\cdot CH\!-\!\!-\!\!-\!\!-\!CH\cdot CO_2H \\ CO_2H\cdot CH\cdot OH \quad COPh \end{matrix}$ (X.)

decomposition and loss of carbon dioxide to give a dibasic acid, $C_{12}H_{10}O_5$. This dibasic acid, which is also obtained by hydrolysis of the ester $C_{19}H_{22}O_7$ with boiling methyl alcoholic potassium hydroxide, is most probably 5-phenyl-2 : 3-dihydrofuran-2 : 3-dicarboxylic acid (XII), since this formula explains its formation from the acid $C_{13}H_{12}O_8$(X), and also accounts for the fact that it

(XI.) $\begin{matrix} CO_2H\cdot CH \\ CO_2H\cdot CH \end{matrix}\!>\!CH\cdot COPh$ $\qquad$ $\begin{matrix} CO_2H\cdot CH\!-\!CH \\ CO_2H\cdot CH \quad\; CPh \\ \qquad\quad \diagdown\; \diagup \\ \qquad\quad\;\; O \end{matrix}$ (XII.)

forms no oxime or hydrazone in the cold, whereas if it were 1-benzoyl*cyclo*propane-2 : 3-dicarboxylic acid (XI), it should yield these derivatives. Moreover, when the acid $C_{12}H_{10}O_5$ is several times recrystallised from boiling water it is converted into an acid of composition $C_{12}H_{12}O_6$, which melts with decomposition at 175—176°. This new acid must be α-phenacyl-β-hydroxysuccinic acid (phenacylmalic acid) (XIII), formed by the opening of the dihydrofuran ring in the acid (XII). It is reconverted into the acid $C_{12}H_{10}O_5$ by repeated crystallisation from a mixture of chloroform and methyl alcohol.

(XIII.) $\begin{matrix} CO_2H\cdot CH\cdot CH_2\cdot COPh \\ CO_2H\cdot CH\cdot OH \end{matrix}$ $\qquad$ $\begin{matrix} CO_2H\cdot C(OH)\cdot CH_2\cdot COPh \\ CO_2H\cdot CH_2 \end{matrix}$ (XIV.)

Again, although the acid $C_{12}H_{10}O_5$ forms no hydrazone with phenylhydrazine in the cold, yet when heated with that reagent in acetic

acid solution it yields the hydrazone $C_{18}H_{18}O_5N_2$ of the acid $C_{12}H_{12}O_6$.

All these results can only be interpreted if the ester $C_{19}H_{22}O_7$ is ethyl 5-phenyl-2 : 3-dihydrofuran-2 : 3 : 4-tricarboxylate; the condensation of ethyl *dl*-dibromosuccinate with ethyl sodiobenzoylacetate can therefore be represented by equation 4.

(4) $\begin{matrix}CO_2Et\cdot CHBr\\ CO_2Et.CHBr\end{matrix} \longrightarrow \begin{matrix}CO_2Et\cdot CH\text{———}C\cdot CO_2Et\\ CO_2Et\cdot CHBr\quad NaO\cdot C\cdot C_6H_5\end{matrix} \longrightarrow$ (VIII.)

It is noteworthy that Ruhemann and Stapleton (J., 1896, **69**, 1383) obtained an ester, $C_{19}H_{22}O_7$, by the action of ethyl sodiobenzoylacetate on both ethyl chloromaleate and ethyl chlorofumarate, which yielded on hydrolysis an acid, $C_{12}H_{12}O_6$, melting with decomposition at 172°, to which they assigned the formula (XIII). In a later paper (J., 1900, **77**, 804), they saw reason to alter it to formula (XIV). It seems probable that the acid $C_{12}H_{12}O_6$ (m. p. 175—176°) obtained by us is identical with that described by Ruhemann and Stapleton and that formula (XIII) is the correct expression.

The condensation of ethyl *meso*-dibromosuccinate with ethyl sodiobenzoylacetate proceeds in an entirely different manner from that of the racemic ester. The main products of the reaction are ethyl dibenzoylsuccinate and an oil, $C_{19}H_{24}O_7$, which was found to be ethyl α-benzoyltricarballylate (XV).

(XV.) $\begin{matrix}CO_2Et\cdot CH\cdot CH(CO_2Et)\cdot COPh\\ CO_2Et\cdot CH_2\end{matrix}$ $\qquad$ $\begin{matrix}CO_2H\cdot CH\cdot CH_2\cdot COPh\\ CO_2H\cdot CH_2\end{matrix}$ (XVI.)

The oil yielded on hydrolysis a dibasic acid, $C_{12}H_{12}O_5$, melting at 163—164°, the most probable formula for which is that of phenacylsuccinic acid (XVI). This acid was first obtained by Emery (*J. pr. Chem.*, 1896, [ii], **53**, 312) from the ester (XV), which was synthesised from ethyl chlorosuccinate and ethyl sodiobenzoylacetate; he gave the melting point as 156—157°. Later Vorländer (*Annalen*, 1906, **345**, 223) obtained the same acid by the oxidation of cinnamylideneacetophenoneacetic ester and he gave the melting point as 160—161°. In order to prove the constitution of the acid obtained by us, ethyl α-benzoyltricarballylate (XV) was synthesised from ethyl fumarate and ethyl sodiobenzoylacetate (equation 5);

(5) $\begin{matrix}CO_2Et\cdot CH\\ CH\cdot CO_2Et\end{matrix} \xrightarrow{CHNa(CO_2Et)\cdot COPh} \begin{matrix}CO_2Et\cdot CH\cdot CH(CO_2Et)\cdot COPh\\ CO_2Et\cdot CH_2\end{matrix}$

on hydrolysis, it yielded an acid identical in every respect with the acid obtained in the condensation of ethyl *meso*dibromosuccinate with ethyl sodiobenzoylacetate, which is thus proved to be phenacylsuccinic acid.

The condensation of ethyl *meso*-dibromosuccinate with ethyl sodiobenzoylacetate seems to proceed in two stages: the first stage consists in the formation of ethyl fumarate and ethyl dibenzoylsuccinate (equation 6) and then the ethyl fumarate adds on ethyl sodiobenzoylacetate to give ethyl α-benzoyltricarballylate (equation 5).

(6) $\begin{matrix}CO_2Et\cdot CHBr\\ CO_2Et\cdot CHBr\end{matrix} \xrightarrow{CHNa(CO_2Et)\cdot COPh} \begin{matrix}CO_2Et\cdot C\\ \|\\ CH\cdot CO_2Et\end{matrix} + \begin{matrix}CO_2Et\cdot CH\cdot COPh\\ CO_2Et\cdot CH\cdot COPh\end{matrix}$

Section D.—The *dl*- and *meso*-dibromosuccinic esters were found to react with sodioacetoacetic ester in a direction similar to that discussed above in the case of the sodium derivative of benzoylacetic ester.

Ethyl *dl*-dibromosuccinate and ethyl sodioacetoacetate interact to give a 95 per cent. yield of an ester, $C_{14}H_{20}O_7$, which might be either ethyl 1-acetyl*cyclo*propane-1 : 2 : 3-tricarboxylate (XVII), or ethyl 5-methyl-2 : 3-dihydrofuran-2 : 3 : 4-tricarboxylate (XVIII).

$\begin{matrix}CO_2Et\cdot CH\\ CO_2Et\cdot CH\end{matrix}\!>\!C<\!\begin{matrix}COMe\\ CO_2Et\end{matrix}$ (XVII.)

$\begin{matrix}CO_2Et\cdot CH-C\cdot CO_2Et\\ CO_2Et\cdot CH\quad\ CMe\end{matrix}$ (XVIII.)

$\begin{matrix}CO_2H\cdot CH\cdot CH_2\cdot COMe\\ CO_2H\cdot CH\cdot OH\end{matrix}$ (XIX.)

This ester was shown to be the dihydrofuran ester (XVIII) by its hydrolysis to acetonylmalic acid (XIX), which can only be derived from the ester (XVIII). Acetonylmalic acid was first obtained by Ruhemann and Tyler (J., 1896, **69**, 530) by the hydrolysis of the condensation product either of ethyl chloromaleate or of ethyl chlorofumarate with ethyl sodioacetoacetate. These authors give the melting point as 146—147° and the acid obtained by us melts at 150°.

Ethyl 5-methyl-2 : 3-dihydrofuran-2 : 3 : 4-tricarboxylate, when left in contact with ammonia, is converted into a substance, $C_{10}H_{14}O_5N_2$, presumably an amide, which is probably identical the amide described by Ruhemann and Tyler (*loc. cit.*).

Ethyl *meso*-dibromosuccinate and ethyl sodioacetoacetate were found to yield ethyl diacetosuccinate and an oil, $C_{14}H_{22}O_7$, which was shown to be ethyl α-acetyltricarballylate (XX) by hydrolysis to acetonylsuccinic acid (XXI).

(XX.) $\begin{matrix}CO_2Et\cdot CH\cdot CH(CO_2Et)\cdot COMe\\ CO_2Et\cdot CH_2\end{matrix}$ $\qquad$ $\begin{matrix}CO_2H\cdot CH\cdot CH_2\cdot COMe\\ CO_2H\cdot CH_2\end{matrix}$ (XXI.)

This acid was obtained by Emery (*J. pr. Chem.*, 1896, [ii], **53**,

310) by the hydrolysis of ethyl α-acetonyl-α′-carboxysuccinate; he gave the melting point as 107°, whilst the acid obtained by us melts at 110°. The anhydride was prepared by distilling the acid in a vacuum as described by Emery.

EXPERIMENTAL.

The Dibromination of Succinic Acid.—Succinyl chloride was prepared and brominated in the manner recommended by R. Meyer and Marx (*Ber.*, 1908, **41**, 2465). The crude dibromosuccinyl chloride was poured into alcohol, water was added, and the ester collected in ether. The main bulk of this ester distilled at 135—145°/10 mm., and partly solidified on standing in ice and salt; the solid was recrystallised from alcohol and was found to be pure ethyl *meso*-dibromosuccinate (m. p. 58°) (Found: Br = 48·0. Calc. for $C_8H_{12}O_4Br_2$, Br = 48·1 per cent.).

The residual oil was redistilled and obtained as an oil, b. p. 137—138°/11 mm., which showed no sign of solidifying on standing in a freezing-mixture. It was ethyl *dl*-dibromosuccinate, containing, no doubt, some of the *meso*-isomeride (Found: Br = 47·9. Calc. for $C_8H_{12}O_4Br_2$, Br = 48·1 per cent.).

The Addition of Bromine to the Esters of Maleic and Fumaric Acids.

Ethyl dl-*Dibromosuccinate.*—To ethyl maleate (50 gms.), in pure dry ether (250 c.c.) cooled by cold water and protected from direct sunlight by a cloth, dry bromine (46·5 gms.) was added drop by drop. When the pale yellow colour of the solution indicated the end of the reaction, the ether solution was washed, first with dilute sulphurous acid to remove bromine, then with dilute sodium carbonate solution to remove acid, and finally with water. After evaporation of the ether, the crude ester was distilled under reduced pressure and *ethyl* dl-*dibromosuccinate* was obtained as an oil which distilled without decomposition at 137—138°/11 mm. and showed no sign of solidifying at −15° (Found: Br = 48·0. $C_8H_{12}O_4Br_2$ requires Br = 48·1 per cent.).

Methyl dl-*Dibromosuccinate.*—This ester, prepared exactly as was the ethyl ester, melted at 43°, was readily soluble in methyl alcohol, and crystallised from ligroin (b. p. 40—60°) in large prisms (Found: Br = 52·5. $C_6H_8O_4Br_2$ requires Br = 52·6 per cent.).

Ethyl meso-*Dibromosuccinate.*—Ethyl maleate was converted completely into ethyl fumarate by boiling gently for an hour with a trace of iodine. An equimolecular weight of dry bromine was added to the cooled liquid and the whole heated on the water-bath to start the reaction, which was then very rapid. The product was poured into ice-water, when the greater part solidified. The

solid was collected and recrystallised from alcohol and, in this way, a 66 per cent. yield of pure *ethyl* meso-*dibromosuccinate* was obtained, m. p. 58° (Found : Br = 48·1. $C_8H_{12}O_4Br_2$ requires Br = 48·1 per cent.).

Methyl meso-*Dibromosuccinate.* This ester was prepared in an exactly similar manner from methyl fumarate except that the bromination was effected in glacial acetic acid solution, as methyl fumarate is a solid (m. p. 102°). The crude product was freed from unchanged methyl fumarate by distillation under reduced pressure; it crystallised from ligroin in prisms, m. p. 65° (Found : Br = 52·7. $C_6H_8O_4Br_2$ requires Br = 52·6 per cent.).

A. *The Condensation of the Dibromosuccinic Esters with the Sodium Derivative of Malonic Ester.*

(1) *The Racemic Esters.*—Sodium (5 gms.) was dissolved in absolute alcohol (80 c.c.), mixed with ethyl malonate (35 gms.), the whole cooled in ice-water, and ethyl *dl*-dibromosuccinate (36 gms.) added gradually, the temperature being kept below 5°. The mixture was kept for an hour and then boiled on the steam-bath for ½ hour. The product was poured into water, the oil extracted with ether and, after evaporation of the ether, fractionated under 11 mm. The following fractions were obtained : (1) below 100°; (2) 100—150° (a few drops only); (3) 180—200°. Fraction (1) consisted of unchanged ethyl malonate; fraction (3) was redistilled and 30 gms. of a colourless oil, b. p. 187°/11 mm., were obtained, which proved to be ethyl *cyclo*propane-1 : 2 : 2 : 3-tetracarboxylate (Found : C = 54·4; H = 6·5. Calc. for $C_{15}H_{22}O_8$, C = 54·5; H = 6·6 per cent.).

Methyl *cyclo*propanetetracarboxylate, obtained in a similar manner from methyl *dl*-dibromosuccinate and methyl malonate, was crystallised from ligroin and melted at 85° (Found : C = 48·1; H = 5·0. Calc., C = 48·1; H = 5·1 per cent.).

(2) *The* meso-*Esters.*—Ethyl *meso*-dibromosuccinate and ethyl sodiomalonate were allowed to react in an exactly similar manner to that described above. A mixture of products was obtained from which ethyl fumarate and ethyl ethanetetracarboxylate were isolated as well as an oil distilling at 190—200°/11 mm., which appeared to be a mixture and was not further examined. More definite results were obtained when the ethyl esters were replaced by the corresponding methyl esters, the preparation being as in (1) : sodium, 5 gms., methyl alcohol, 80 c.c.; methyl malonate, 29 gms.; methyl *meso*-dibromosuccinate, 32 gms. After 12 hours, the reaction mixture was poured into water, the solid which separated filtered off, and the oil extracted with ether. The residual oil from

the ether extraction was fractionated under reduced pressure, when it yielded methyl malonate and an oil distilling at 175—178°/9 mm., which was hydrolysed by boiling with hydrochloric acid. Evaporation to dryness left tricarballylic acid, m. p. 163° (Found: C = 40·8; H = 4·7. Calc., C = 40·9; H = 4·6 per cent.). The oil must then have been methyl α-carboxytricarballylate, formed by the addition of methyl malonate to methyl fumarate.

The solid product of this condensation was dried and extracted with boiling ligroin (b. p. 60—80°) when, on cooling, methyl *cyclo*propane-1 : 2 : 2 : 3-tetracarboxylate separated and was identified by its melting point (85°) and by hydrolysis to the tetrabasic acid. The residue from the ligroin extraction was recrystallised from benzene; it melted at 138° and was proved to be methyl ethanetetracarboxylate by direct comparison.

In another experiment the reaction mixture was allowed to stand for an hour only; in this case very little of the oil was formed, but methyl fumarate was isolated from the solid product by distillation under reduced pressure.

dl-cyclo*Propane*-1 : 2 : 2 : 3-*tetracarboxylic Acid* (I).—This acid, easily obtained from its esters by boiling with hydrochloric acid, crystallises from water as the dihydrate, $C_7H_6O_8,2H_2O$, m. p. 100° (Found: C = 32·9; H = 4·0. $C_7H_{10}O_{10}$ requires C = 33·0; H = 3·9 per cent.). The anhydrous acid is obtained by heating the hydrated acid at 110—115° (Found: H_2O = 14·21. $C_7H_6O_8,2H_2O$ requires H_2O = 14·17 per cent.). It melts at 198—200° with decomposition and evolution of carbon dioxide (Found: C = 38·5; H = 2·7. $C_7H_6O_8$ requires C = 38·5; H = 2·7 per cent.).

As this acid was shown by resolution (see below) to be the *trans*- or *dl*-acid, an attempt was made to convert it into the *cis*- or *meso*-isomeride. The acid (2 gms.) was heated with acetic anhydride (20 c.c.) in a sealed tube for 3 hours at 150—160°. The acetic acid and anhydride were then distilled off under reduced pressure and the residual oil was dissolved in hot water. The solution was evaporated and allowed to crystallise, when crystals were obtained which, after dehydration, melted at 198°, and consisted of the *trans*-acid.

Resolution of dl-cyclo*Propane*-1 : 2 : 2 : 3-*tetracarboxylic Acid*.—The tetracarboxylic acid (18 gms.) was dissolved in hot water (500 c.c.), mixed with brucine (140 gms.) and, after heating on the steam-bath, the excess of brucine was filtered off and the filtrate allowed to cool. The brucine salt which separated was collected, redissolved in hot water (500 c.c.), and the clear solution allowed to cool; crystallisation began at 68°, and at 45° the brucine salt was collected and washed with warm water. This salt was then recrystallised several times in a similar manner, the crystallised salt being always

collected when the temperature of the solution had fallen to 45°. After each recrystallisation the rotation was observed in a 2-dcm. tube, the amount taken being made up to 20 c.c. with pure chloroform.

No.	1	2	3	4	5
Gm. of salt	0·1324	0·1390	0·1612	0·1525	0·1674
α obs.	− 0·63°	− 0·64°	− 0·70°	− 0·65°	− 0·72°
$[\alpha]_D^{18°}$	−47·6°	−46·05°	−43·42°	−43·05°	−43·01°

The pure brucine salt of the dextro-acid has therefore $[\alpha]_D^{18°} = 43·01°$ (Found: N = 6·05. $C_7H_6O_8,4C_{23}H_{26}O_4N_2,2H_2O$ requires N = 6·1 per cent.).

This pure salt was decomposed by adding ammonia to the warm aqueous solution, and the filtrate from the precipitated brucine evaporated almost to dryness. The calculated amount of hydrochloric acid was added to decompose the ammonium salt and the mixture evaporated to dryness. The residue was extracted with cold, carefully purified, acetone, and after removing the main bulk of the acetone, the residual oil was left in a vacuum over phosphorus pentoxide until it crystallised. The crystals were dried on porous plate and then recrystallised from water (Found: C = 38·7; H = 2·7. $C_7H_6O_8$ requires C = 38·5; H = 2·7 per cent.; 0·1315 gm., made up to 20 c.c. with water, gave α = 1·40° in a 2-dcm. tube at 18°; whence $[\alpha]_D^{18°} = 106·5°$).

d-cyclo*Propane*-1 : 2 : 2 : 3-*tetracarboxylic acid* melts at 195—196° with decomposition and evolution of carbon dioxide to give inactive *trans-cyclo*propane-1 : 2 : 3-tricarboxylic acid. The *dl*-acid melts at 198—200°, and a mixture of the *d*-acid and the *dl*-acid at 165°.

trans-cyclo*Propane*-1 : 2 : 3-*tricarboxylic acid* (III) was prepared by heating the tetracarboxylic acid at 200° until no more carbon dioxide was evolved and was recrystallised from hydrochloric acid; m. p. 220° (Found: C = 41·3; H = 3·5. $C_7H_6O_8$ requires C = 41·4; H = 3·4 per cent.).

The acid was recovered unchanged after heating with acetic anhydride for 3 hours at 180—190° in a sealed tube and dissolving the anhydro-acid so formed in hot water.

B. *The Condensation of the Dibromosuccinic Esters with the Sodium Derivative of Cyanoacetic Ester.*

(1) *The Racemic Ester.*—Sodium (5 gms.) was dissolved in absolute alcohol (80 c.c.), mixed with ethyl cyanoacetate (25 gms.), and ethyl *dl*-dibromosuccinate (36 gms.) added to the ice-cold mixture drop by drop and with constant stirring. The reaction mixture was kept over-night and then boiled on the steam-bath for an hour.

The product was poured into water and the oil extracted with ether, when 26 gms. of an oil distilling at 200—205°/18 mm. were obtained (Found: N = 5·9. $C_{13}H_{17}O_6N$ requires N = 4·9 per cent.). The oil was hydrolysed by boiling with hydrochloric acid, the clear solution evaporated to dryness, the solid residue extracted with acetone and the acetone solution filtered from ammonium chloride and evaporated.

The acid obtained in this way proved to be *dl-cyclo*propanetetracarboxylic acid; consequently the ester formed in the condensation must have been *ethyl 2-cyano*cyclo*propane*-1 : 2 : 3-*tricarboxylate* (V).

(II) *The* meso-*Ester*.—The condensation of ethyl *meso*-dibromosuccinate with ethyl sodiocyanoacetate was carried out exactly as in the case of the racemic ester. The oil (22 gms.) distilling at 210—215°/18 mm. was hydrolysed with hydrochloric acid and the acid formed identified as tricarballylic acid. The crude acid was recrystallised from a mixture of methyl alcohol and chloroform, when it was obtained in sugar-like crystals, m. p. 163° (Found: C = 41·0; H = 4·6. $C_6H_8O_6$ requires C = 40·9; H = 4·6 per cent. 0·1651 Gram neutralised 28·4 c.c. of *N*/10-sodium hydroxide, where the same amount of tricarballylic acid would require 28·1 c.c.).

The residual syrup after the removal of the tricarballylic acid was left over sulphuric acid until it crystallised. The small amount (1 gm.) of crystalline material so obtained proved to be *dl-cyclo*propanetetracarboxylic acid.

C. *The Condensation of the Dibromosuccinic Esters with the Sodium Derivative of Benzoylacetic Ester.*

(1) *The Racemic Ester*.—Sodium (5 gms.) was dissolved in alcohol (80 c.c.), mixed with ethyl benzoylacetate (41 gms.), and ethyl *dl*-dibromosuccinate (36 gms.) gradually added to the ice-cold mixture; the product was boiled on the steam-bath until neutral and then poured into water.

The whole was extracted with ether and the oil obtained, after evaporation of the ether, fractionated under reduced pressure, when ethyl benzoylacetate came over first and then the temperature rose rapidly and a thick, yellow oil (34 gms.), distilling at 227—230/12 mm., was obtained. This oil was proved to be *ethyl 5-phenyl-2 : 3-dihydrofuran-2 : 3 : 4-tricarboxylate* (VIII) by analysis (Found: C = 62·6; H = 5·9. $C_{19}H_{22}O_7$ requires C = 62·9; H = 6·1 per cent.) and by an examination of the products of hydrolysis.

When the ester was allowed to stand with methyl alcoholic potassium hydroxide (20 per cent.) for 2 days, a potassium salt crystallised

out which was dissolved in water and treated with a hot solution of lead nitrate. The precipitated lead salt was collected, washed with hot water, suspended in water, and decomposed with hydrogen sulphide; the lead sulphide was filtered off and the aqueous solution evaporated. The solid acid so obtained was recrystallised from water, when it melted with decomposition at 142—143° and was found to be *α-hydroxy-γ-benzoyltricarballylic acid* (X) (Found: C = 52·9; H = 4·1. $C_{13}H_{12}O_8$ requires C = 52·6; H = 4·0 per cent. 0·2691 Gram neutralised 26·9 c.c. of *N*/10-sodium hydroxide, whereas $C_{13}H_{12}O_8$ would require 27·2 c.c.). The acid is very soluble in water and alcohol, insoluble in benzene and chloroform; above its melting point it decomposes with loss of carbon dioxide to give 5-phenyl-2 : 3-dihydrofuran-2 : 3-dicarboxylic acid (XII) (m. p. 183°), which is described below.

The ester $C_{19}H_{22}O_7$ was next hydrolysed by boiling with methyl alcoholic potassium hydroxide and, after evaporation of the alcohol, the aqueous solution was acidified, when an oil was precipitated which soon solidified. This crude acid was recrystallised several times from methyl alcohol–chloroform, when it melted sharply at 182—183°. It was shown to be *5-phenyl-2 : 3-dihydrofuran-2 : 3-dicarboxylic acid* by analysis (Found: C = 61·3; H = 4·6. $C_{12}H_{10}O_5$ requires C = 61·5; H = 4·7 per cent.), and by an examination of its properties. It did not yield an oxime on treatment with hydroxylamine hydrochloride and potassium hydroxide in the cold. It formed no hydrazone with phenylhydrazine in the cold, but, when heated with this reagent in acetic acid solution, it yielded a hydrazone, which after recrystallisation from aqueous alcohol and finally from toluene melted at 210° and proved to be the hydrazone of phenacylmalic acid (Found: N = 8·15. $C_{18}H_{18}O_5N_2$ requires N = 8·18 per cent.).

Phenacylmalic acid (XIII) itself was formed from the phenyldihydrofurandicarboxylic acid by repeated recrystallisation of the latter from boiling water. It melts with decomposition at 175—176° (Found: C = 58·6; H = 4·9. $C_{12}H_{12}O_6$ requires C = 57·2; H = 4·8 per cent.). Ruhemann and Stapleton (J., 1896, **69**, 1383) give the melting point of this acid as 172°. Repeated crystallisation of phenacylmalic acid from methyl alcohol–chloroform converts it back into the phenyldihydrofurandicarboxylic acid (m. p. 183°).

(II). *The* meso-*Ester*.—The condensation of ethyl *meso*dibromosuccinate with ethyl sodiobenzoylacetate was performed exactly as in the case of the racemic ester. The oil precipitated by pouring the reaction mixture into water partly solidified; the solid was collected, washed with ether, and recrystallised from alcohol, when

it melted at 130° and proved to be ethyl dibenzoylsuccinate (Found: C = 69·0; H = 5·9. Calc., C = 69·1; H = 5·8 per cent.). The oily filtrate from this was extracted with ether and, after evaporation of the ether, was fractionated under 11 mm.; the first fraction (90—100°) proved to be ethyl fumarate, since on hydrolysis it yielded fumaric acid. The main bulk came over between 200° and 240° with considerable decomposition due to the presence of ethyl dibenzoylsuccinate. This fraction deposited a bright yellow solid which was almost insoluble in the usual solvents, but crystallised from acetone in golden-yellow plates, m. p. 285° (Found: C = 74·3; H = 3·5. $C_{18}H_{10}O_4$ requires C = 74·5; H = 3·5 per cent.). This substance is evidently identical with the unnamed substance obtained by Knorr and Scheidt (*Ber.*, 1894, **27**, 1167) by heating ethyl dibenzoylsuccinate at 270—290°. After filtering off this yellow solid, the oil was redistilled and boiled at 220—225°/11 mm.

This oil was hydrolysed by boiling with alcoholic potassium hydroxide; water was added, the alcohol evaporated, and the solution acidified. The precipitated oil gradually solidified and the crude acid was pressed on porous plate and recrystallised from ether, from which it separated in needles, m. p. 162—163°; this acid proved to be phenacylsuccinic acid (XVI) (Found: C = 61·01; H = 5·13. Calc. for $C_{12}H_{12}O_5$, C = 61·01; H = 5·08 per cent.).

In order to prove the constitution of this acid, phenacylsuccinic acid was synthesised in the following manner: ethyl fumarate (1 mol.) was added to ethyl sodiobenzoylacetate (1 mol.) in alcohol and, after 12 hours, the product was poured into dilute acid and the oil extracted with ether. After evaporation of the ether, the oil was distilled and the main bulk consisted of *ethyl α-benzoyltricarballylate*, b. p. 220—225°/12 mm. (Found: C = 62·7; H = 6·4. $C_{19}H_{24}O_7$ requires C = 62·6; H = 6·6 per cent.). This ester was hydrolysed by boiling with alcoholic potassium hydroxide and the acid so obtained recrystallised from ether. It melted at 165° and from its mode of formation must be phenacylsuccinic acid; a mixture of it and the acid obtained in the condensation described above melted at 163°.

The *oxime* of phenacylsuccinic acid was prepared by mixing the solution of the acid in sodium hydroxide with hydroxylamine hydrochloride, and was isolated by acidifying and extracting the solution with ether. It separated from a mixture of ethyl acetate and ligroin in needles, m. p. 147—148° (Found: N = 5·57. $C_{12}H_{13}O_5N$ requires N = 5·57 per cent.). The oxime is readily soluble in water, alcohol, or chloroform, insoluble in benzene, ligroin, etc.

The *phenylhydrazone* was made by treating an aqueous solution

of the acid with phenylhydrazine acetate and crystallised from a mixture of chloroform and ligroin, and finally from toluene, in needles, m. p. 164—165° (Found : N = 8·7. $C_{18}H_{18}O_4N_2$ requires N = 8·7 per cent.).

D. *The Condensation of the Dibromosuccinic Esters with the Sodium Derivative of Acetoacetic Ester.*

(I) *The Racemic Ester.*—Sodium (5 gms.) was dissolved in alcohol (80 c.c.) and mixed with ethyl acetoacetate (28 gms.), the solution cooled in ice, and ethyl *dl*-dibromosuccinate (36 gms.) gradually added. After standing for an hour the reaction mixture was boiled on the steam-bath till neutral and then poured into water. The oil was extracted with ether and fractionally distilled under 18 mm., when ethyl acetoacetate came over first; the temperature then rose and the main bulk distilled at 190—195° and was found to consist of *ethyl* 5-*methyl*-2 : 3-*dihydrofuran*-2 : 3 : 4-*tricarboxylate* (XVIII) (Found : C = 55·6; H = 6·5. $C_{14}H_{20}O_7$ requires C = 56·0; H = 6·6 per cent.).

The ester was hydrolysed by methyl alcoholic potassium hydroxide, the product diluted with water, the alcohol evaporated, enough hydrochloric acid added to decompose the potassium salt, and the solution evaporated to dryness. The residue was extracted with pure acetone in a Soxhlet apparatus, and after evaporation of the acetone a clear gum was left which eventually crystallised on standing in a desiccator. The crystals were drained on porous plate and recrystallised from water. The pure acid melted at 150° and proved to be acetonylmalic acid (XIX) (Found : C = 44·3; H = 5·3. Calc. for $C_7H_{10}O_6$, C = 44·3; H = 5·3 per cent.). Ruhemann (J., 1896, **96**, 530) states that this acid melts at 147°.

When the ester $C_{14}H_{20}O_7$ was left to stand with concentrated ammonia, crystals of an amide separated which after recrystallisation from water melted at 195° (Found : N = 11·5. Calc. for $C_{10}H_{14}O_5N_2$, N = 11·5 per cent.). Ruhemann (*loc. cit.*) had already prepared this amide and discussed its constitution.

(II) *The* meso-*Ester.*—Ethyl *meso*-dibromosuccinate was condensed with ethyl sodioacetoacetate in exactly the same manner as the racemic ester. The oil obtained from this condensation deposited crystals on standing which were identified as ethyl diacetosuccinate by the melting point (88°), and by comparison with a specimen of this substance. The residual oil was distilled under reduced pressure, when the main bulk came over at 175—185°/12 mm. and proved to be ethyl α-acetyltricarballylate (XX) (Found : C = 55·7; H = 7·1. $C_{14}H_{22}O_7$ requires C = 55·6; H = 7·3 per cent.).

The acid obtained by hydrolysing this ester with hydrochloric acid, after crystallisation from water, melted at 110° and was identified as acetonylsuccinic acid (XXI) (Found: C = 48·2; H = 5·7. $C_7H_{10}O_5$ requires C = 48·3; H = 5·7 per cent.). It was compared with a specimen of this acid prepared by synthesising ethyl α-acetyltricarballylate from ethyl fumarate and ethyl sodioacetoacetate in alcohol solution and subsequent hydrolysis (compare Ruhemann and Browning, J., 1898, **73**, 727).

Acetonylsuccinic anhydride was prepared by distilling the free acid under reduced pressure; the solid distillate crystallised from a mixture of chloroform and ligroin in needles, m. p. 95—96° (Found: C = 53·9; H = 5·0. $C_7H_8O_4$ requires C = 53·8; H = 5·1 per cent.).

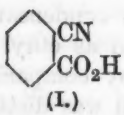
In conclusion, one of us (H. R. I.) wishes to thank the Warden and Fellows of New College, Oxford, for a Senior Scholarship which enabled him to take part in this work. All the analyses were carried out by Mr. F. Hall.

DYSON PERRINS LABORATORY,
OXFORD. [*Received, May 20th*, 1924.]

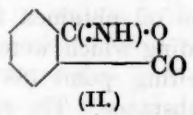
CCXXX.—*Ring-chain Tautomerism. Part X. Inhibited Tautomerism.*

By FRANK DICKENS, LAURENCE HORTON, and JOCELYN FIELD THORPE.

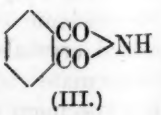
ONE of the most remarkable examples of the change from an open-chain compound to the isomeric ring complex through the movement of a hydrogen atom is supplied by a β-cyano-acid, for example, *o*-cyanobenzoic acid (I). It seems that this acid can only be isolated under special conditions (Braun and Tcherniac, *Ber.*, 1907, **40**, 2713), and that it passes into its isomeride phthalimide (III) at its melting point; a change which evidently takes place through the oximino-derivative (II).



(I.)



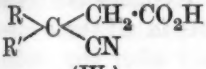
(II.)

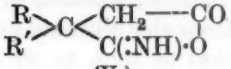


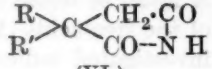
(III.)

It is not our purpose in this paper to discuss the change from the oximino-form (II) to the imido-form (III). The chief interest from our point of view lies in the change from the compound (I) to the compound (II), which is of the ring-chain type, and the

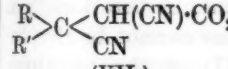
study of which should, therefore, yield further information regarding the nature of this phenomenon. It will be remembered that in the previous parts of this series evidence has been brought forward showing that the tetrahedral angle formed normally by any two carbon valencies can be altered by the attachment of groups or ring complexes to the other two valencies and that, in this way, chains joined to the valencies forming the altered angle are rendered more or less prone to form rings depending on the extent to which the angle is changed. It follows, therefore, that in a series of substances of the general formula (IV), where R R′ are hydrogen atoms, alkyl groups or the carbon atoms of a ring complex, valuable

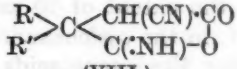

(IV.)

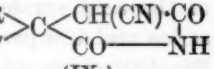

(V.)


(VI.)

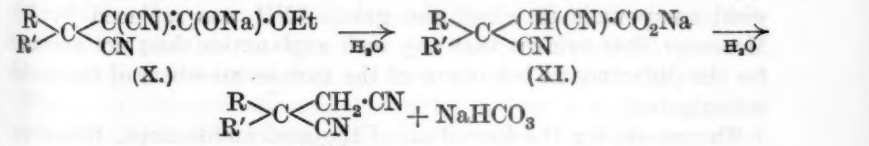
evidence would be obtained as to the occurrence of tautomerism of the ring-chain type between the isomerides (IV) and (V) over a wide range of conditions, but, pending the discovery of some means by which these compounds can be prepared in quantity, we have directed our attention to a series of analogous compounds which are more readily available, namely, the dicyano-acids of formula (VII).


(VII.)


(VIII.)


(IX.)

We find that the sodium derivatives of these esters (X) react when the solution is boiled, yielding the sodium salts of type (XI) (compare Thorpe, J., 1900, **77**, 923). Incidentally, the reaction does not stop here, but yields, ultimately, the dinitriles (XII) in good yield.


(X.) (XI.) (XII.)

The series investigated contained the compounds of type (XI) having R R′ as dimethyl, *cyclo*hexane and *cyclo*heptane respectively, the sodium salts having the metal replaced by hydrogen under precisely similar conditions. In these circumstances, we were interested to find that in no instance could any trace either of the acids (VII) or of their oximino-derivatives (VIII) be isolated from the products of the reactions, the only compounds obtained as ultimate products being the acid amides (XIV) and the imides

(IX). Moreover, there was a remarkable difference in the proportions in which these compounds were found in the reaction products of the various series investigated, as is shown by the following table :

Series RR′.	(Acid amide XIV).	(Imide IX).
*cyclo*Hexane.	100 per cent.	nil.
Dimethyl.	70 per cent.	30 per cent.
*cyclo*Heptane.	nil.	100 per cent.

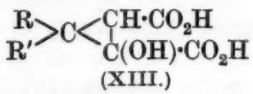
The acid amide (XIV) and the imide (IX) are the ultimate products, not the intermediate compounds, produced in the reactions.

In seeking a theoretical explanation for these remarkable results it must be noted : (i) that the absence of any recognisable traces of the free acids (VII) from the ultimate products in all three cases investigated indicates that as soon as, or shortly after the mobile hydrogen atoms are introduced they pass on to nitrogen to form the oximino-derivatives (VIII); (ii) that the absence of any recognisable traces of the oximino-compounds indicates that these substances are also removed as soon as or shortly after they are formed; (iii) that the formation of the imide (IX) in the dimethyl and *cyclo*heptane series shows that the oximino-compounds are removed owing to their transformation into the imides by the molecular rearrangement mentioned on page 1834; (iv) that the production of the acid amides to the extent of 70 per cent. in the dimethyl series and 100 per cent. in the *cyclo*hexane series cannot be due to the hydrolysis of either the cyano-acids (VII) or the oximino-compounds (VIII), because, in the former case, the resistance of the relevant cyano-groups to hydrolytic action has already been shown by the stability of the sodium salts (p. 1831), and, in the latter, the compound in question is an imino-ether of the Pinner type and would, presumably, react towards hydrolysing agents to yield compounds in which the group =NH was replaced by =O. Moreover, it is evident that any such explanation does not account for the difference in behaviour of the various members of the series investigated.

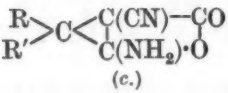
The reason for the formation of the acid amide must, therefore, be sought elsewhere and we suggest that the following explanation fits all the facts so far discovered.

It will be remembered that one of the most striking examples of the effect produced by the deflection of the tetrahedral angle by the *cyclo*hexane ring is provided by the stability and ease of formation of the hydroxy-ring acid (XIII) and it will be noticed that the oximino-compound (*b*) can be converted into a similar substance (*c*) by the passage of the mobile hydrogen atom across the ring. If such a tendency existed, it would be greatest in the *cyclo*hexane

series and less in the dimethyl series in which the angle deflection is not sufficiently great to confer stability on the hydroxy ring acid of type (XIII).

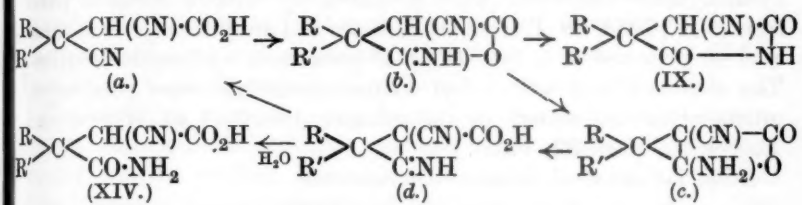


(XIII.)



(*c*.)

The amino-compound (*c*) can now pass by hydrogen movement into the imino-acid (*d*), which is, however, unstable * and, in the absence of hydrolysing agents, changes by movement of the second mobile hydrogen atom into the cyano-acid (*a*). If, on the other hand, a hydrolysing agent is present the acid amide (*e*) is formed. The cycle of changes can therefore be represented as under :



(*a*.) (*b*.) (IX.)

(XIV.) (*d*.) (*c*.)

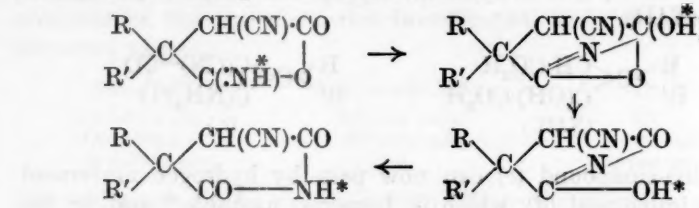
It follows, therefore, that in the absence of any marked tendency for the oximino-compound (*b*) to be converted into the imide (IX), and in the absence of hydrolytic agents, the four compounds (*a*), (*b*), (*c*), and (*d*) will form a cycle of substances which should ultimately yield an equilibrium mixture of the four components. We have not as yet been able to realise these conditions, for even in the *cyclo*hexane series, in which the absence of the imide from the reaction product shows that the rate at which the oximino-compound (*b*) changes into the amino-compound (*c*) must be greater than the rate at which it passes into the imide, it has not been found possible to establish conditions which will prevent the removal of the imino-acid (*d*) from the cycle by hydrolysis.

These experiments also supply further evidence that the *cyclo*heptane ring is not uniplanar. Had it been so, it is to be expected that the *cyclo*heptane derivatives described in this paper would have been more closely related in their behaviour to those of *cyclo*hexane.

Finally, it may be mentioned that the change from (*b*) to (IX) is

* The instability of the complex has been shown by a number of experiments (compare Beesley, Ingold, and Thorpe, J., 1915, **107**, 1080; Ingold, Sako, and Thorpe, J., 1922, **121**, 1177).

itself an example of the formation and fission of rings of the type associated with ring-chain tautomerism :



(The mobile hydrogen is marked with an asterisk.)

Experimental.

Condensation of Cyanohydrins with Ethyl Sodiocyanoacetate.—The cyanohydrins employed were prepared by Ultée's method (*Rec. trav. chim.*, 1909, **28**, 1) from the ketones and anhydrous hydrocyanic acid in presence of a few drops of potassium hydroxide solution. The condensations with ethyl sodiocyanoacetate were conducted, unless otherwise stated, in the manner described by Higson and Thorpe (J., 1906, **89**, 1455).

Ethyl 1-*Cyano*cyclo*hexane*-1-*cyanoacetate*, $C_5H_{10}{>}C(CN)\cdot CH(CN)\cdot CO_2Et$.—The well-cooled suspension of ethyl sodiocyanoacetate prepared from ethyl cyanoacetate (28 grams) and sodium (5·5 grams) in absolute alcohol (75 grams) was gradually added, with vigorous stirring, to a well-cooled solution of *cyclo*hexanone cyanohydrin (31 grams) in 40 c.c. of absolute alcohol. The reacting mixture was allowed to stand for 24 hours at room temperature, poured into 400 c.c. of water, and carefully acidified with dilute hydrochloric acid. A heavy oil was precipitated which solidified completely on cooling. It crystallised from benzene–light petroleum (b. p. 50—60°) in colourless prisms, m. p. 54°, b. p. 210—212°/22 mm. (yield 70 per cent.) (Found : C = 65·56; H = 7·47. $C_{12}H_{16}O_2N_2$ requires C = 65·45; H = 7·27 per cent.).

1-*Carboxy*cyclo*hexane*-1-*acetic Acid.*—The cyano-ester was boiled with four times its weight of dilute hydrochloric acid (25 per cent.) until completely dissolved. The cooled solution deposited a crystalline acid which after one recrystallisation from water melted at 132° [Found : C = 58·30; H = 7·63; *M* (dibasic) = 186. Calc., C = 58·06; H = 7·53 per cent; *M* = 186] (compare Norris and Thorpe, J., 1921, **119**, 1199).

1-*Cyano*cyclo*hexane*-1-*acetonitrile* (R R′ = C_5H_{10}; XII) and *Sodium* 1-*Cyano*cyclo*hexane*-1-*cyanoacetate* (R R′ = C_5H_{10}; XI).—The sodium derivative of the cyano-ester dissolves in water giving a clear solution from which, on careful acidification, the unchanged

ester is precipitated. If, however, the aqueous solution is slowly evaporated on the water-bath, a mixture of the dinitrile, sodium salt, and sodium hydrogen carbonate is formed. It is possible by a suitable choice of conditions to vary the relative proportions of the dinitrile and sodium salt, the formation of the dinitrile being favoured by the use of a slight deficit of sodium (90 per cent. of calculated), the sodium salt on the other hand being produced in optimum amounts by the use of a slight excess of the metal (110 per cent. of calculated). The yield is about 75 per cent. in each case. Ethyl 1-cyano*cyclo*hexane-1-cyanoacetate (22 grams) was dissolved in 30 c.c of absolute alcohol and a solution of the appropriate amount of sodium in 40 c.c. of absolute alcohol added. Water (120 c.c.) was added and the solution evaporated. The *dinitrile* was separated from the product by means of ether, in which it alone was soluble, and after recrystallisation from dilute alcohol was obtained as lustrous plates, m. p. 84·5° (Found: C = 72·78; H = 8·28. $C_9H_{12}N_2$ requires C = 72·97; H = 8·11 per cent.).

The residual mixture of sodium 1-cyano*cyclo*hexane-1-cyanoacetate and sodium hydrogen carbonate was extracted with hot alcohol and, on cooling, the extract deposited the sodium salt in silvery leaflets which softened at 145° and melted at 149°. The salt is moderately soluble in alcohol and in water; its solution is neutral to litmus (Found: Na = 10·58. $C_{10}H_{11}O_2N_2Na$ requires Na = 10·74 per cent.). The *silver* salt, prepared from the sodium salt, is a white, microcrystalline precipitate (Found: Ag = 36·16. $C_{10}H_{11}O_2N_2Ag$ requires Ag = 36·12 per cent.). When boiled in ether suspension with an excess of ethyl iodide, a quantitative yield of the cyano-ester (m. p. 54°) is obtained.

Acidification of the sodium salt. When an aqueous solution of the sodium salt is cautiously acidified with dilute hydrochloric acid an oil is precipitated which is soluble in excess of mineral acid. The solution so formed slowly deposits a crystalline substance which is 1-*carbamyl*cyclo*hexane*-1-*cyanoacetic acid* (R R′ = C_5H_{10}; formula XIV, p. 1833).—It crystallises from water in small prisms which melt at 90° and decompose at 100° (Found: C = 57·52; H = 6·95; N = 13·55. $C_{10}H_{14}O_3N_2$ requires C = 57·14; H = 6·67; N = 13·33 per cent.). The yield is practically quantitative. An aqueous solution of the sodium salt was cautiously acidified with the calculated quantity of 5*N*-hydrochloric acid in the presence of ether, and the ethereal extract was divided into two halves. One half, on being shaken with a saturated solution of sodium hydrogen carbonate, yielded an alkaline extract from which a copious precipitate of *sodium* 1-*carbamyl*cyclo*hexane*-1-*cyanoacetate*,

$$C_5H_{10}{>}C(CO{\cdot}NH_2){\cdot}CH(CN){\cdot}CO_2Na,$$

separated on standing. It melted at 105—108° after recrystallisation from alcohol, and when acidified in aqueous solution gave the amide-acid melting at 90°, the identity being confirmed by direct comparison. The yield was quantitative. The other half of the ether extract was mixed with an ether solution containing the theoretical quantity of aniline, when the *aniline* salt of 1-*cyano*cyclo*hexane*-1-*cyanoacetic acid*, $C_5H_{10}>C(CN)\cdot CH(CN)\cdot CO_2H, PhNH_2$, was at once formed as a crystalline precipitate; it melted at 98° (Found: C = 67·57; H = 6·52. $C_{16}H_{19}O_2N_3$ requires C = 67·37; H = 6·67 per cent.). The salt was formed in quantitative yield and was readily converted into an acid by means of dilute mineral acids. The product obtained in this way was, however, only the acid amide melting at 90°. An attempt was made to ascertain the nature of the compound in the ether solution which had given rise to the aniline salt, but the solution on evaporation yielded an acidic gum from which nothing crystalline could be obtained. It was, however, analysed in the crude condition (Found: C = 62·21; H = 7·50. $C_{10}H_{12}O_2N_2$ requires C = 62·50; H = 6·25 per cent.).

The Imide of 1-*Carboxy*cyclo*hexane*-1-*cyanoacetic Acid* (R R′ = C_5H_{10}; formula IX, p. 1831).—This substance is formed when the amide acid melting at 90° is digested with glacial acetic acid for ½ hour. It is separated by evaporation, rubbing the product with water, and recrystallising the solid residue from benzene and petroleum (b. p. 100—110°). It forms rectangular prisms, m. p. 123—124° (Found: C = 62·74; H = 6·45; N = 14·66. $C_{10}H_{12}O_2N_2$ requires C = 62·50; H = 6·25; N = 14·58 per cent.). It may also be prepared from the sodium salt of the cyano-acid on treatment with acetyl chloride. The imide is soluble in aqueous sodium carbonate solution and is unaffected on boiling with water for 3 hours.

α-*Carbamyl*-1-*carboxy*cyclo*hexane*-1-*acetic acid*,

$$C_5H_{10}>C(CO_2H)\cdot CH(CO\cdot NH_2)\cdot CO_2H,$$

is formed when a solution of the cyano-imide (m. p. 123—124°) (3·4 grams) in 50 per cent. aqueous potassium hydroxide (8 c.c.) is boiled under reflux for 2 hours. The acid, which is obtained on acidification, separates from water in white crystals, m. p. 126° (decomp.) (Found: N = 6·44. $C_{10}H_{15}O_5N$ requires N = 6·11 per cent.).

The *imide* of 1-*carboxy*cyclo*hexane*-1-*acetic acid* (formula VI; R R′ = C_5H_{10}) is obtained when the above amido-acid is heated above its melting point. It separates from dilute alcohol as silky needles, m. p. 145° (Found: C = 64·77; H = 7·93; N = 8·9. $C_9H_{13}O_2N$ requires C = 64·67; H = 7·78; N = 8·38 per cent.). It was identified by comparison with a specimen which had been

prepared by the action of carbamide on the anhydride of 1-carboxy*cyclo*hexane-1-acetic acid. The imide is unaffected by boiling with water for 3 hours and on hydrolysis with aqueous sodium hydroxide yields 1-carboxy*cyclo*hexane-1-acetic acid.

1-*Carbamyl*cyclo*hexane*-1-*acetamide*,

$$C_5H_{10}{>}C(CO{\cdot}NH_2){\cdot}CH_2{\cdot}CO{\cdot}NH_2,$$

is produced when a solution of 1-cyano*cyclo*hexane-1-acetonitrile in an equal weight of concentrated sulphuric acid is allowed to stand for 12 hours. It is obtained on pouring the solution into water and is purified by recrystallisation from alcohol, when it yields silvery scales, m. p. 201° (Found: C = 58·79; H = 8·70. $C_9H_{16}O_2N_2$ requires C = 58·70; H = 8·70 per cent.). The diamide yields 1-carboxy*cyclo*hexane-1-acetic acid on treatment with nitrous acid.

The Action of Heat on 1-*Carbamyl*cyclo*hexane*-1-*cyanoacetic Acid*.—The products formed by the action of heat on the above acid vary widely with the conditions. Two examples can be given:

(1) *At 72—74° for ½ hour*. The product was a neutral gum from which an acid (present as the ammonium salt) and a neutral substance were isolated. The former, when purified through the calcium salt, proved to be 1-carboxy*cyclo*hexane-1-acetic acid, m. p. 132° (see p. 1834). The latter was found to be the *imide* of *α-carbamyl*-1-*carboxy*cyclo*hexane*-1-*acetic acid*,

$$C_5H_{10}{>}C{<}\begin{matrix}CH(CO{\cdot}NH_2){\cdot}CO\\ CO\text{———}NH\end{matrix}.$$

It crystallises from water in clusters of long prisms, m. p. 152° (decomp.) (Found: C = 56·66; H = 6·78. $C_{10}H_{14}O_3N_2$ requires C = 57·14; H = 6·67 per cent.). The imide is completely hydrolysed to the sodium salt of 1-carboxy*cyclo*hexane-1-acetic acid on prolonged boiling with sodium hydroxide solution.

(2) *At 80—84° for 4 hours*. The gum formed in this instance yielded a solid material when rubbed with water, which, when purified by means of chloroform and recrystallised from a mixture of ethyl alcohol and benzene, formed glistening leaflets, m. p. 175° (Found: C = 58·67; H = 8·42; N = 7·98. $C_9H_{15}O_3N$ requires C = 58·38; H = 8·11; N = 7·57 per cent.). The analysis and the formation of the acid melting at 132° on hydrolysis with either alkali or nitrous acid point to the formula $C_5H_{10}{>}C(CO_2H){\cdot}CH_2{\cdot}CO{\cdot}NH_2$ for this substance.

Three other compounds were isolated: the dinitrile melting at 84·5° (see p. 1835), the imide melting at 123—124°, and 1-carboxy*cyclo*hexane-1-acetic acid melting at 132° (see p. 1834).

Sodium αβ-Dicyano-ββ-dimethylpropionate (R R′ = Me_2; formula XI, p. 1831).—A solution of sodium (2·44 grams) in 35 c.c. of absolute

alcohol was added to a solution of ethyl αβ-dicyano-ββ-dimethylpropionate (18 grams; Higson and Thorpe, *loc. cit.*) in 20 c.c. of absolute alcohol and the whole diluted with 25 c.c. of water. The alcohol and water were distilled off under diminished pressure at 60—70° and the residual gum in the flask dissolved in about 10 c.c. of water. The solution was then exhaustively extracted with ether to remove the dinitrile (yield about 40 per cent. of the theoretical). The aqueous solution contained the sodium salt mixed with sodium hydrogen carbonate. It was mixed with an equal volume of ether and acidified with the calculated quantity of 5*N*-hydrochloric acid with vigorous shaking. The solution was then exhaustively extracted with ether and the extract washed with a saturated solution of sodium hydrogen carbonate. The ether left no residue on evaporation. The alkaline liquid was cautiously acidified in the presence of ether and extracted with this solvent, the extract yielding on evaporation a gum, which rapidly solidified. It consisted of an acid and a neutral component which were separated by shaking the ethereal solution with aqueous sodium hydrogen carbonate. The ethereal solution on evaporation yielded the *imide* of *α-cyano-ββ-dimethylsuccinic acid* (R R′ = Me_2; formula IX) in 30 per cent. yield calculated on the sodium salt. It separates from benzene in small prisms, m. p. 116° (Found: C = 55·02; H = 5·32. $C_7H_8O_2N_2$ requires C = 55·26; H = 5·26 per cent.).

β-Carbamyl-α-cyano-ββ-dimethylpropionic Acid (R R′ = Me_2; formula XIV, p. 1833).—The alkaline solution gave an oil on being rendered acid which slowly solidified. After recrystallisation from water, it melted with decomposition at 142° (Found: C = 49·52; H = 6·01. $C_7H_{10}O_3N_2$ requires C = 49·41; H = 5·88 per cent.). The acid was completely converted into the imide melting at 116° when boiled with three times its weight of glacial acetic acid for 5 minutes. The yield of the acid was approximately 70 per cent. calculated on the sodium salt used.

as-*Dimethylsuccinonitrile* (R R′ = Me_2; formula XII, p. 1831).—Although this substance is obtained as a by-product in the previous experiment, it is best prepared in quantity by the following process. A solution of sodium (2·2 grams) in absolute alcohol (35 c.c.) was added to a solution of ethyl αβ-dicyano-ββ-dimethylpropionate (18 grams) in 25 c.c. of alcohol and poured into 120 c.c. of water. The mixture was rapidly distilled until an oil passed over which solidified in the condenser. At this point the distillation was stopped and the residue in the flask extracted with ether. The dinitrile left on evaporating the ether crystallised from the solvent in rectangular prisms, m. p. 68°. It has previously been described by Hell and Rothberg (*Ber.*, 1889, **32**, 1740) as a water-clear liquid

(Found: C = 66·95; H = 7·49. $C_6H_8N_2$ requires C = 66·67; H = 7·47 per cent.).

as-Dimethylsuccinamide, $CMe_2(CO\cdot NH_2)\cdot CH_2\cdot CO\cdot NH_2$, is obtained when a solution of the dinitrile in an equal weight of concentrated sulphuric acid is allowed to stand at room temperature for 12 hours and then poured into water. The diamide does not separate owing to its solubility, but can be isolated by neutralising the solution with ammonia, evaporating to dryness, and extracting the residue with hot acetone. It crystallises from benzene–petroleum (b. p. 40—50°) in small prisms, m. p. 153° (Found: C = 50·32; H = 8·22. $C_6H_{12}O_2N_2$ requires C = 50·00; H = 8·33 per cent.). On treatment with nitrous acid the diamide yields *as*-dimethylsuccinic acid, m. p. 140°.

Ethyl 1-*Cyano*cyclo*heptane*-1-*cyanoacetate*,

$$C_6H_{12}{>}C(CN)\cdot CH(CN)\cdot CO_2Et.$$

The cyanohydrin of *cyclo*heptanone cannot be distilled owing to decomposition into hydrocyanic acid and the ketone. The crude substance was therefore used in the condensation with ethyl sodiocyanoacetate, the conditions being the same as in the case of the *cyclo*hexane compound. The ethereal solution of the condensation product was washed with aqueous sodium carbonate and yielded, on evaporation, the ester as a colourless oil, b. p. 201°/13 mm. (Found: C = 66·55; H = 7·96. $C_{13}H_{18}O_2N_2$ requires C = 66·67; H = 7·69 per cent.).

α-*Cyano*cyclo*heptylideneacetic Acid*, $C_6H_{12}{>}C{:}C(CN)\cdot CO_2H$.—The sodium carbonate washings from the foregoing operation were acidified and extracted with ether. The extract yielded an oil which solidified on keeping for several weeks in a vacuum desiccator. After recrystallisation from petroleum (b. p. 40—60°), it was obtained in fine needles, m. p. 91° [Found: C = 67·04; H = 7·71; *M* (monobasic) = 179. $C_{10}H_{13}O_2N$ requires C = 67·04; H = 7·26 per cent.; *M* = 179). The same acid was obtained when suberone was condensed with ethyl sodiocyanoacetate by the method of Harding, Haworth, and Perkin (J., 1908, **93**, 1944); it was isolated from the acid portion of the reaction product. Its occurrence in the cyanohydrin condensation is doubtless due to the presence of unchanged ketone in the initial material.

Sodium 1-*Cyano*cyclo*heptane*-1-*cyanoacetate* (R R′ = C_6H_{12}; formula XI, p. 1831).—A solution of 2·43 grams of sodium in 40 c.c. of absolute alcohol was added to a solution of 23·4 grams of ethyl 1-cyano*cyclo*heptane-1-cyanoacetate in 30 c.c. of alcohol, and the whole poured into 70 c.c. of water. The solution was gently evaporated to dryness on the water-bath, during which operation a strong odour of suberone was noticed. The dry solid residue was

extracted with dry ether in a Soxhlet apparatus, the ether extract yielding 1-*cyano*cyclo*heptane*-1-*acetonitrile* (R R′ = C_6H_{12}; formula XII, p. 1831) on evaporation. It crystallises from dilute alcohol in stout prisms, m. p. 58° (Found: C = 73·84; H = 8.64. $C_{10}H_{14}N_2$ requires C = 74·07; H = 8·64 per cent.). The residue in the Soxhlet apparatus consisted of a mixture of sodium 1-cyano-*cyclo*heptane-1-cyanoacetate and sodium hydrogen carbonate. Separation could not be effected satisfactorily owing to the tendency for the sodium salt to break down into the dinitrile and sodium hydrogen carbonate. The mixture was therefore acidified with dilute hydrochloric acid and extracted with ether. The ether solution contained no acid product but only the *imide* of 1-*carboxy*-cyclo*heptane*-1-*cyanoacetic acid* (R R′ = C_6H_{12}; formula IX, p. 1831), which, after recrystallisation from water, was obtained in glistening plates, m. p. 130° (Found: C = 63·75; H = 6·99. $C_{11}H_{14}O_2N_2$ requires C = 64·07; H = 6·80 per cent.). No trace of the acid amide (XIV) could be detected among the products of the reaction.

The Imide of 1-*Carboxy*cyclo*heptane*-1-*acetic Acid* (formula VI; R R′ = C_6H_{12}).—A solution of the pure cyano-ester in an equal volume of concentrated sulphuric acid was kept at room temperature for 2 days. The mixture was then diluted with an equal volume of water and boiled from 6 to 8 hours. The cooled solution was extracted with ether, the ethereal extract washed with sodium carbonate solution and then with water, dried, and evaporated. A white solid was obtained which, after recrystallisation from petroleum (b. p. 60—80°), formed slender needles, m. p. 116° (Found: C = 66·19; H = 8·52. $C_{10}H_{15}O_2N$ requires C = 66·30; H = 8·29 per cent.).

1-*Carboxy*cyclo*heptane*-1-*acetic Acid*, $C_6H_{12}{>}C(CO_2H){\cdot}CH_2{\cdot}CO_2H$. —The sodium carbonate washings from the above hydrolysis were acidified and extracted with ether. The extract yielded a solid which, after recrystallisation from water, melted at 153° [Found: C = 60·08; H = 8·00; *M* (dibasic) = 199. $C_{10}H_{16}O_4$ requires C = 60·00; H = 8·00 per cent.; *M* = 200].

Part of the expense of this research was met by grants from the Government Grant Committee of the Royal Society and from the Chemical Society, for which we desire to express our thanks.

THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, March 27th*, 1924.]

CCXXXI.—*The Thermal Decomposition of Chlorine Monoxide. Part II. Relation to the General Theory of Bimolecular Reactions.*

By CYRIL NORMAN HINSHELWOOD and JOSEPH HUGHES.

ONE of the most interesting problems of chemical dynamics is the determination of the mechanism by which molecules are activated or brought into the reactive condition. Isolated molecules appear to be incapable of chemical change, since no unimolecular reactions are known to proceed in the gaseous state. The two reactions which were supposed to be examples of such changes have been shown in the one case not to be unimolecular and in the other case not to be homogeneous; the hypothesis of activation by radiation therefore becomes pointless, at least on the grounds which led Perrin originally to suggest it. In bimolecular homogeneous reactions activation can be interpreted in a simple and illuminating way. From Bodenstein's data on the thermal decomposition of hydrogen iodide (*Z. physikal Chem.*, 1899, **29**, 295) Lewis (J., 1918, **113**, 471) calculated the actual number of molecules reacting per second under specified conditions of pressure and temperature. The total number of collisions between hydrogen iodide molecules under the same conditions was also calculated. Twice this number gave the number of molecules which might have reacted if every collision had been fruitful. From the influence of temperature upon the reaction velocity the joint heat of activation, Q, of two gram-molecules of hydrogen iodide was calculated. From the results it appears that the relation

$$\frac{\text{number of effective collisions}}{\text{total number of collisions}} = e^{-Q/RT} \quad . \quad . \quad . \quad (1)$$

is satisfactorily fulfilled.

If this were generally true for bimolecular gaseous reactions, we could say that every collision between two molecules the joint energy of which exceeds an amount Q, calculable from the temperature coefficient of the reaction velocity, leads to reaction. We are thus concerned with simple thermal activation by collision, and no further hypotheses are necessary. Whether Q represents internal energy or kinetic energy of translation is probably immaterial, since at the moment of collision redistribution of energy takes place.

Burk and Hinshelwood have recently ascertained that the bimolecular decomposition of nitrous oxide is a true homogeneous

In Part I, line 7 of summary, for "rate of reaction" read "time required for a given fraction of the reaction."

reaction and that the above relation is fairly satisfactorily fulfilled in this case also (*Proc. Roy. Soc.*, 1924, *A*, **106**, 284).

Chlorine monoxide was shown in Part I of this investigation (J., 1923, **123**, 2730) to undergo a homogeneous decomposition, bimolecular in nature, but consisting of consecutive stages probably involving an unknown oxide of chlorine as an intermediate product. This complication hindered the direct testing of the equation (1). The test would have been particularly interesting in this case, since chlorine monoxide is a gas in which explosion waves are readily set up, the products of reaction having under such conditions energy sufficient to activate fresh molecules. It seemed not impossible, therefore, that even in the slow decomposition quite long " reaction chains " might be set up, the activation of a single pair of molecules being sufficient to cause the decomposition of a chain of some hundreds or thousands. If this were so, equation (1) would not be even approximately true.

We have now, however, in a manner described below, put equation (1) to the test. From the equation we find Q to be 22,000 calories, whilst the value found experimentally from the temperature coefficient is 21,000 calories.

The following table is interesting: T_{abs} = temperature at which k, the bimolecular velocity coefficient, has the same value for each reaction (namely, 0·0914 gm.-mol. per litre per second).

Reaction. Thermal decomposition.	Q from equation (1).	Q from temperature coefficient.	$T_{abs.}$
$2N_2O$	55,000	58,500	956°
$2HI$	43,900	44,000	760
$2Cl_2O$	22,000	21,000	384

The parallelism between Q and the absolute temperature at which the reaction proceeds at a given rate, combined with the agreement between the observed and calculated values of Q, seems to dispose conclusively of accidental coincidence, and to render it certain that bimolecular reactions can be interpreted in terms of simple thermal activation by collision.

Further Experiments on the Consecutive Stages of the Reaction.

These may be described before passing to the main portion of the paper.

The relative proportions of chlorine monoxide and chlorine in a mixture of the two gases may be found by absorbing in potassium iodide solution, when the following reactions take place:

$$Cl_2 + 2I' = I_2 + 2Cl'.$$
$$Cl_2O + H_2O + 4I' = 2I_2 + 2Cl' + 2OH'.$$

If chlorine monoxide decomposed directly into chlorine and oxygen, the rate of decomposition could be measured by analysing samples of gas at different times, and a decomposition–time curve would be found of the same form as that showing the increase of pressure with time. If, however, intermediate products are formed, the reaction of which with potassium iodide differs from that of chlorine monoxide and chlorine, then a curve of a different form would be expected. We have made experiments with two forms of apparatus. In one, samples of the gas were expelled at different times by running in sulphuric acid; in the other, no displacing liquid was employed, but the pressure in the decomposition vessel was allowed to mount up until it was sufficient to expel a convenient sample of gas when released. The apparent percentage of chlorine monoxide in each sample was calculated on the assumption that nothing but chlorine and chlorine monoxide reacted with the potassium iodide, and curves were plotted showing the apparent rate of disappearance of chlorine monoxide. With both types of apparatus curves were obtained differing from the curves of pressure increase, in which the pressure rises steadily with time, by having in the middle a flat portion over which the apparent percentage of chlorine monoxide does not change, although the reaction, as shown by the pressure increase, proceeds steadily. This would indicate the production of some intermediate oxide the action of which on potassium iodide compensates for the falling concentration of chlorine monoxide.

We had hoped to obtain quantitative information about the nature of the intermediate product in this way, but, unfortunately, although very concordant analyses could be obtained both near the beginning and near the end of the reaction, in the neighbourhood of the flat portion samples of the gas taken at the same time gave rather discordant results—presumably because the reaction of the intermediate compound with potassium iodide is less regular than that of chlorine monoxide and chlorine. The results, therefore, must be regarded only as an interesting confirmation by chemical means of the conclusions already arrived at from the kinetic measurements in Part I. Curves and detailed results are therefore withheld.

The Influence of Temperature.—The decomposition takes place in consecutive stages, and it does not follow that the influence of temperature will be the same at all stages of the reaction. It was proposed to investigate the extent to which the temperature coefficient of the reaction differed at different stages.

Experiments were carried out with mixtures of chlorine monoxide and air at various temperatures, a large decomposition bulb with a sulphuric acid manometer being employed. Pressure–time curves were plotted in each case and the times required for the

reaction to proceed from 20—30 per cent., 30—40 per cent., etc., were read off. These times were all reduced to an initial pressure of chlorine monoxide equal to 2000 mm. of sulphuric acid, the time required for the reaction to complete any fraction of its course being inversely proportional to the initial pressure of chlorine monoxide. (The initial pressures of chlorine monoxide were all much lower in these experiments than those in the experiments recorded in Part I, but the results of the two sets tallied with one another completely at the same temperature.) The average of all corresponding times in the different experiments at a given temperature was taken. A further reduction was necessary to make times at different temperatures comparable, since equal pressures at different absolute temperatures correspond to slightly different concentrations. The necessary correction for this was made. Suppose t_{20}^{40} be the time required for the reaction to proceed from 20 to 40 per cent., then $1/t_{20}^{40}$ is a measure of the velocity of reaction over this range. The logarithm of $1/t$ plotted against the reciprocal of the absolute temperature (T) gives a straight line, the slope of which gives the heat of activation. The logarithms of $1/t_{20}^{40}$, $1/t_{40}^{60}$, and $1/t_{60}^{80}$ were separately plotted against $1/T$, and the three curves obtained were found to be practically parallel. (Two of them happen also to be coincident, but this is of no significance.) This means that there is no detectable variation in the heat of activation in the different stages of the reaction—a fact which enables us, as will be seen in the next section, to apply the theory of bimolecular reactions in spite of the complication of consecutive reactions.

The following two tables contain the experimental results. All times are corrected to an initial concentration at the actual temperature corresponding to 2000 mm. H_2SO_4 at 383·0° Abs.

Abs. temp.	Number of expts. made.	Average values. t_{20}^{30} min.	t_{30}^{40} min.	t_{40}^{50} min.	t_{50}^{60} min.	t_{60}^{70} min.	t_{70}^{80} min.
333·2°	1	616	533	533	553	826	1395
352·5	3	131	121	111	119	136	172
372·0	2	27·8	24·5	25·8	26·3	31·2	41·7
383·0	8	11·1	10·6	11·3	13·2	15·9	20·8
404·3	4	2·9	2·4	2·3	2·5	3·2	4·4

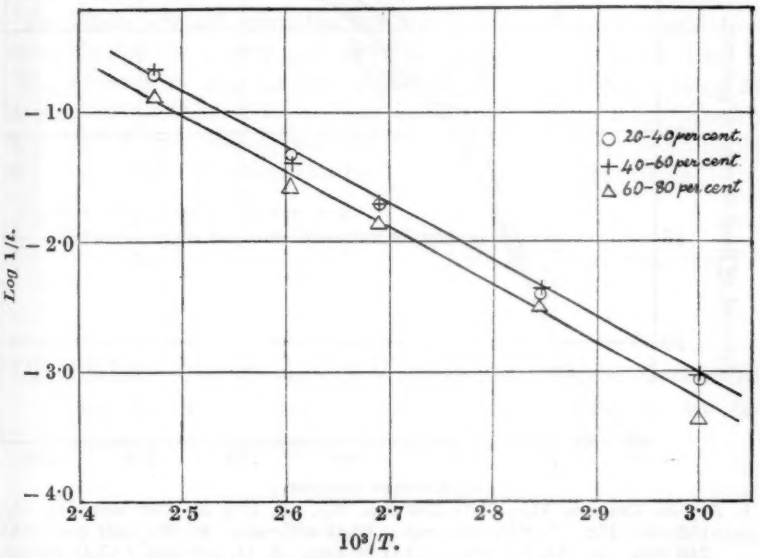
The curves are plotted from the following figures:

T.	$1/T\times10^3$.	t_{20}^{40}.	t_{40}^{60}.	t_{60}^{80}.	$\log 1/t_{20}^{40}$.	$\log 1/t_{40}^{60}$.	$\log 1/t_{60}^{80}$.
333·2°	3·000	1150	1100	2220	−3·061	−3·041	−3·346
352·5	2·845	252	230	308	−2·401	−2·362	−2·489
372·0	2·688	52·3	52·1	72·9	−1·719	−1·717	−1·863
383·0	2·611	21·7	24·5	36·7	−1·337	−1·389	−1·565
404·3	2·473	5·3	4·8	7·6	−0·724	−0·681	−0·881

From the slope of these curves the heat of activation for any stage of the reaction is found to be approximately 21,000 calories per 2 gram-molecules.

Application of the Theory of Bimolecular Reactions.—The relation between velocity coefficient and heat of activation is an exponential one, k being a function of $e^{-Q/RT}$. The decomposition of chlorine monoxide proceeds in stages, but appears to be bimolecular throughout its course. Two values of k must be involved; they cannot be separated mathematically, but as the separate stages of the reaction are not sharply defined these two values must be of the same order of magnitude. From the nature of the relation between k and Q

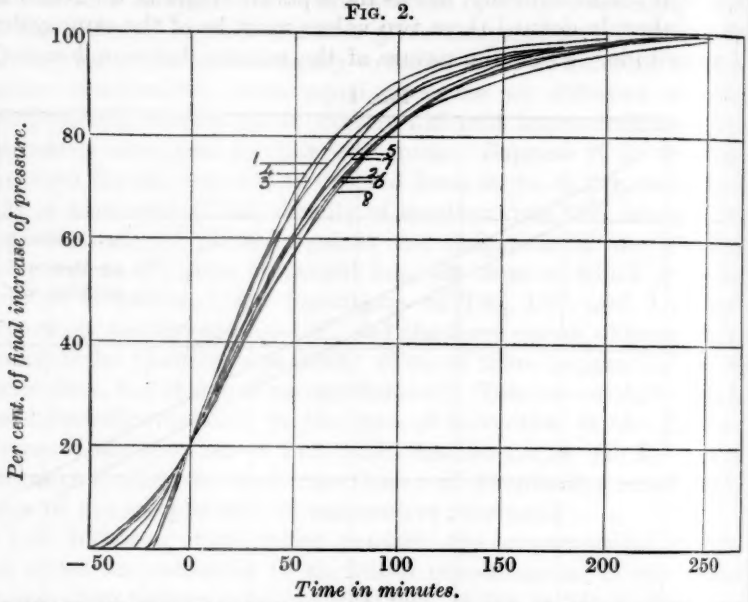
FIG. 1.



it is clear that it is permissible to average two values of k which do not differ very greatly, whilst it would not be permissible to take the average of two values of Q which differed appreciably. Since, however, we have found that the value of Q is constant throughout the reaction within the limit of experimental error, we may investigate the relation between this nearly constant value of Q and an average value of k. When it is borne in mind that comparatively small changes in Q may alter the corresponding values of k by many powers of ten it will be seen that slight uncertainties about the true average value of k are not very serious. We accordingly calculate k by reading off from a curve the time required for the reaction to proceed from 40 per cent. to 80 per cent., and substituting this time in a simple bimolecular equation.

We now proceed in the manner of Lewis (*loc. cit.*). From k the actual number of molecules reacting per c.c. per second at atmospheric pressure may be found. Taking the molecular diameter of the chlorine monoxide molecule as $4{\cdot}8 \times 10^{-8}$ cm., the number of collisions per c.c. per second at atmospheric pressure is found from the relation $N = \sqrt{2}\pi\sigma^2\bar{u}n^2$, where σ = molecular diameter, $\bar{u}$ = mean square velocity, and n = number of molecules per c.c. Since each collision involves two molecules, by doubling this number we

FIG. 2.



1. *Dry air* 494 *mm.* Hg; Cl_2O 250 *mm.* Hg. 2. *Dry air* 604 *mm.* Hg; Cl_2O 142 *mm.* Hg. 3. CO_2 355 *mm.*; Cl_2O 406 *mm.* 4. CO_2 500 *mm.*; Cl_2O 246 *mm.* 5. CO_2 658 *mm.*; Cl_2O 90 *mm.* 6. O_2 558 *mm.*; Cl_2O 206 *mm.* 7. O_2 583 *mm.*; Cl_2O 186 *mm.* 8. CO_2 484 *mm.*; Cl_2O 280 *mm.*

get the number of molecules which would react if all were activated. The ratio $\frac{\text{number actually reacting per c.c. per sec.}}{\text{number entering into collision per c.c. per sec.}}$ is the fraction of collisions which are fruitful. If most of the collisions between molecules possessing jointly energy in excess of the heat of activation are fruitful, this ratio can be equated to $e^{-Q/RT}$. We may then solve for Q and compare the value obtained with the experimental value. The results are given on p. 1847.

The average value, 22,000 calories, is as near to the experimental value, obtained from the temperature coefficient, 21,000 calories, as can well be expected. The significance of this agreement has already been pointed out.

Abs. temp.	Number of molecules reacting per c.c. per sec. at atmospheric pressure.	Number of molecules colliding per c.c. per sec. at atmospheric pressure.	Heat of activation.
333·2°	$1·2 \times 10^{15}$	$3·1 \times 10^{29}$	21,900
352·5	$6·7 \times 10^{15}$	$2·9 \times 10^{29}$	21,900
372·0	$2·6 \times 10^{16}$	$2·7 \times 10^{29}$	22,100
383·7	$5·7 \times 10^{16}$	$2·4 \times 10^{29}$	22,000
404·3	$2·25 \times 10^{17}$	$2·3 \times 10^{29}$	22,100
		Average	22,000

Influence of Foreign Gases.—It has already been found that the reaction is not appreciably affected by chlorine or oxygen.

Fig. 2 shows the inappreciable effect of air, carbon monoxide, and carbon dioxide.

The times are all corrected for the initial pressure of chlorine monoxide and the curves plotted in the manner described in Part I.

The absence of any marked influence of such different gases as oxygen, carbon monoxide, and carbon dioxide, which might absorb the energy of the reaction products, in itself renders very improbable the existence of " reaction chains " in the slow decomposition.

PHYSICAL CHEMISTRY LABORATORY,
BALLIOL COLLEGE AND TRINITY COLLEGE,
OXFORD.

[*Received, June 26th*, 1924.]

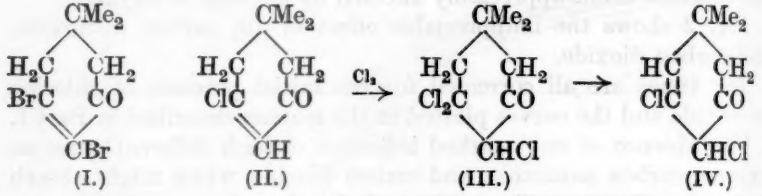
CCXXXII.—*Conversion of Hydroaromatic into Aromatic Compounds. Part I. Action of Chlorine on* 5-*Chloro*-1 : 1-*dimethyl*-Δ^4-cyclo*hexen*-3-*one.*

By LEONARD ERIC HINKEL.

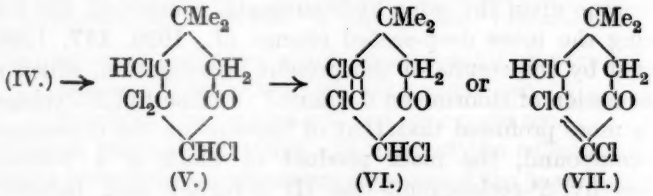
THE fact that there is a divergence between the action of chlorine and bromine upon the same hydroaromatic compound, the former producing the more deep-seated change (J., 1920, **117**, 1296), is supported by the results of the present investigation, which show that the action of chlorine on 5-chloro-1 : 1-dimethyl-Δ^4-*cyclo*hexen-3-one is more profound than that of bromine on the corresponding bromo-compound, the main product of which is 4 : 5-dibromo-1 : 1-dimethyl-Δ^4-*cyclo*hexen-3-one (I) (Crossley and Renouf, J., 1914, **105**, 169).

When well-cooled 5-chloro-1 : 1-dimethyl-Δ^4-*cyclo*hexen-3-one (II) is treated with chlorine, the product consists of a liquid which on distillation in a vacuum yields mainly a liquid dichlorodimethyl-*cyclo*hexenone. As in the case of the bromine reaction (*loc. cit.*), the first action results in the formation of a trihalogen compound (III), which readily loses halogen acid. Under the conditions of

the experiment this loss takes place, not at the carbon atoms 4 and 5 as would be expected, but at 5 and 6, 4 : 5-*dichloro*-1 : 1-*dimethyl*-Δ^5-cyclo*hexen*-3-*one* (IV) being produced (compare Hinkel and Williams, J., 1922, **121**, 2498). This substance is readily transformed by simple means into 5-chloro-*o*-3-xylenol (Hinkel, Collins, and Ayling, J., 1923, **123**, 2968) and 6-*chloro*-o-4-*xylenol* respectively. The constitution of the latter was proved by its synthesis from 5-nitro-*o*-3-xylidine through 6-chloro-4-nitro-*o*-xylene and 6-chloro-*o*-4-xylidine.



If chlorine in excess be allowed to react with 5-chloro-1 : 1-dimethyl-Δ^4-*cyclo*hexen-3-one at the ordinary temperature, a vigorous action ensues, resulting primarily in the formation of a trichlorodimethyl*cyclo*hexenone, together with a very small amount of a tetrachlorodimethyl*cyclo*hexenone. The same trichloro-ketone is obtained when the dichloro-ketone (IV) is chlorinated in chloroform solution. Apparently, therefore, under the influence of the heat of reaction, the compound (III), which is only stable at low temperatures, rapidly decomposes into the dichlorodimethyl*cyclo*hexenone (IV). This combines readily with chlorine to yield an unstable compound (V), which immediately evolves hydrogen chloride. This loss may occur in two ways, giving rise to a trichlorodimethyl-*cyclo*hexenone (VI or VII).

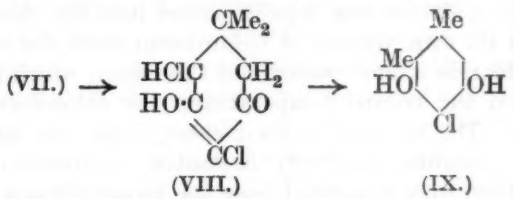


The trichlorohexenone is a solid which is stable to heat and unaffected by chlorine. In these respects it bears a strong resemblance to 4 : 5-dichloro-1 : 1-dimethyl-Δ^4-*cyclo*hexen-3-one (Hinkel and Williams, J., 1922, **121**, 2498), containing the group $ClC\lessdot^{CCl\cdot}_{CO\cdot}$ which appears to have a stabilising effect on the compound (compare Crossley and Le Sueur, J., 1903, **83**, 114). Consequently

the trichlorodimethyl*cyclo*hexenone is better represented by formula VII, which also contains this group.

The transformations of the trichlorodimethyl*cyclo*hexenone accord well with this view. It was readily converted by sulphuric acid into a dichloroxylenol which on treatment with chlorine gave trichloro-*o*-4-xylenol, and by quinoline into a dichloroxylenol which combined with chlorine with great readiness, yielding, not the expected trichloro-*o*-3-xylenol, but a tetrachloroxylenol containing apparently a chlorinated methyl group. Although the constitutions of these dichloroxylenols have not yet been established, the compounds are probably 5 : 6-dichloro-*o*-4-xylenol and 4 : 5-dichloro-*o*-3-xylenol, respectively.

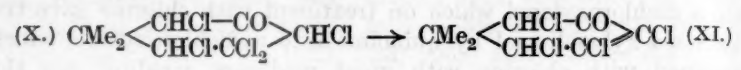
A very similar transformation took place under the influence of alcoholic potassium hydroxide, but in this case the more energetic reagent readily replaced a chlorine atom by hydroxyl, giving rise to a chlorodihydroxyxylene. The 5-chlorine atom in 4 : 5-dichloro-1 : 1-dimethyl-Δ^4-*cyclo*hexen-3-one (Hinkel and Williams, *loc. cit.*) and in 5-chloro-1 : 1-dimethyl-Δ^4-*cyclo*hexen-3-one (Crossley and Le Sueur, J., 1903, **83**, 118) can readily be replaced by hydroxyl, in the one case by means of sulphuric acid, and in the other by alcoholic potassium hydroxide. Therefore, arguing from analogy, it would seem that in the above transformation the first action of the alcoholic potassium hydroxide is the replacement of chlorine by hydroxyl in position 5, yielding a dichloro-derivative (VIII) of dimethyldihydroresorcinol, which then undergoes further transformation by the alcoholic potassium hydroxide into an aromatic compound (IX), the constitution of which would seem best to be described by 4-chloro-3 : 5-dihydroxy-*o*-xylene.



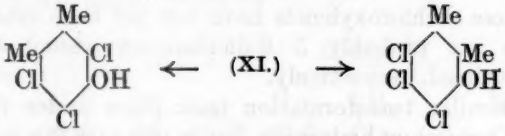
The tetrachlorodimethyl*cyclo*hexenone is readily transformed under the influence of sulphuric acid and also by heat alone, yielding in the former case a mixture of trichloro-*o*-3- and -*o*-4-xylenols, and in the latter case trichloro-*o*-4-xylenol only.

The formation of the tetrachloro-ketone cannot be ascribed to the further chlorination of the trichloro-ketone (VII), since chlorine has no apparent action on the latter compound, even in boiling chloroform solution. It is probable that during the vigorous chlorination of the dichloro-ketone (IV) the unstable intermediate

compound (V) is further chlorinated to a very small extent (compare Armstrong and Lowry, J., 1902, **81**, 1469), and the resulting compound (X), readily losing hydrogen chloride, gives rise to the tetrachlorodimethyl*cyclo*hexenone (XI):



Such a constitution would account for the transformation into the trichloro-*o*-4- and -*o*-3-xylenols.



When the transformation is carried out by means of alcoholic potassium hydroxide, a somewhat strange rearrangement occurs, similar in nature to some previously recorded (Crossley and Renouf, *loc. cit.*) and for which no adequate explanation can be offered.

Although the amount of aromatic compound thus obtained was too small to permit of thorough purification, nevertheless the results of its analysis and that of its benzoyl derivative clearly indicate it to be a dichloroxylenol. The synthesis of the chloro-*o*-xylenols is in progress, and it is hoped thereby to establish the constitution of the xylenols encountered in this investigation.

Experimental.

3 : 4 : 5-*Trichloro*-1 : 1-*dimethyl*-Δ^4-cyclo*hexen*-3-*one* (VII).

Preparation by Chlorination of 5-Chloro-1 : 1-*dimethyl*-Δ^4-cyclo*hexen*-3-*one*.—Chlorine was rapidly passed into the chlorohexenone (40 gms. in its own volume of chloroform) until the evolution of hydrogen chloride almost ceased and the liquid, which had become hot, regained the normal temperature; the chloroform was then evaporated. The viscous, yellow residue, kept over sodium hydroxide in a vacuum, gradually deposited colourless crystals (29 grams). These were separated from the liquid (filtrate A), rapidly washed with well-cooled light petroleum, and recrystallised from light petroleum, 3 : 4 : 5-*trichloro*-1 : 1-*dimethyl*-Δ^4-cyclo*hexen*-3-*one* separating in stout prisms, m. p. 61° (Found: Cl = 46·8. $C_8H_9OCl_3$ requires Cl = 46·8 per cent.). It is readily soluble in the cold in most of the common organic solvents, cannot be further chlorinated in chloroform solution, and boils with gradual decomposition, evolving hydrogen chloride and finally carbonising.

Action of Alcoholic Potassium Hydroxide.—A solution of potassium hydroxide was gradually added to an alcoholic solution of the

trichlorohexenone until the supernatant liquid remained alkaline after gently heating on a water-bath for a few minutes. After removal of the alcohol, the mixture was acidified and steam-distilled. The solid product which passed over was crystallised from aqueous alcohol, 4-*chloro*-3 : 5-*dihydroxy*-o-*xylene* separating in white, glistening plates, m. p. 123° (Found : Cl = 20·64. $C_8H_9O_2Cl$ requires Cl = 20·58 per cent.).

The *dibenzoyl* derivative, prepared in the usual manner, crystallised from alcohol in short needles, m. p. 137° (Found : Cl = 9·19. Calc., Cl = 9·33 per cent.).

Action of Sulphuric Acid.—Five grams of the chloro-ketone were heated with 10 c.c. of sulphuric acid on the water-bath until the first brisk evolution of hydrogen chloride almost ceased, and then for 10 minutes at 110—120°. The mixture, after dilution, was steam-distilled and the solid obtained by extraction of the distillate with ether was purified by treatment with the minimum of hot light petroleum (b. p. 60—80°), in which a small part was insoluble; this was not further examined. The soluble portion was purified by several crystallisations from light petroleum (b. p. 40—60°), 5 : 6-*dichloro*-o-4-*xylenol* separating in clumps of radiating needles, m. p. 102° (Found : Cl = 36·63. $C_8H_8OCl_2$ requires Cl = 37·18 per cent.). It is very soluble in the cold in most organic solvents. When treated with chlorine in light petroleum solution, it readily yields trichloro-*o*-4-xylenol, m. p. 182·5°, identical with that described on p. 1853.

The *benzoyl* derivative of the dichloroxylenol crystallised from alcohol or light petroleum (b. p. 60—80°) in transparent prisms, m. p. 94° (Found : Cl = 23·97. Calc., Cl = 24·07 per cent.).

Action of Quinoline.—A mixture of 5 gms. of the trichloro-ketone and 10 c.c. of quinoline was heated for 30 minutes at 170°, acidified with sulphuric acid, and steam-distilled. The ether extract of the distillate was shaken with acid to remove traces of admixed quinoline, and the product, after removal of ether, crystallised from light petroleum (b. p. 40—60°), 4 : 5-*dichloro*-o-3-*xylenol* separating in fine, stellate masses, m. p. 95° (Found : Cl = 36·98. $C_8H_8OCl_2$ requires Cl = 37·18 per cent.). It combines readily with chlorine in chloroform solution, yielding a tetrachloro-derivative, which crystallises from alcohol in transparent, acicular crystals, m. p. 127·5° (Found : Cl = 54·19. $C_8H_6OCl_4$ requires Cl = 54·6 per cent.).

The *benzoyl* derivative of the dichloroxylenol, prepared in the usual manner, is obtained as a viscous mass, which is soluble in hot alcohol and separates on cooling as an oily liquid which only solidifies on long standing. It crystallises from light petroleum

in colourless, transparent crystals, m. p. 128° (Found: Cl = 23·6. Calc., Cl = 24·03 per cent.).

4 : 5-*Dichloro*-1 : 1-*dimethyl*-Δ^5-cyclo*hexen*-3-*one* (IV).

Preparation by Chlorination of 5-*Chloro*-1 : 1-*dimethyl*-Δ^4-cyclo*hexen*-3-*one at a Low Temperature.*—Chlorine was passed into the chlorohexenone (40 gms. in 40 c.c. of well-cooled chloroform), hydrogen chloride being rapidly evolved towards the end of the reaction, when the solution became yellow. The viscid, colourless liquid obtained after removal of the chloroform did not deposit crystals even after long standing in a vacuum over sodium hydroxide. It was distilled, and the fraction, b. p. 110—130°/13 mm., after several redistillations, yielded 4 : 5-*dichloro*-1 : 1-*dimethyl*-Δ^5-cyclo*hexen*-3-*one*, a colourless liquid with a camphoraceous odour, b. p. 120—121°/13 mm. (Found: Cl = 37·1. $C_8H_{10}O_2Cl$ requires Cl = 36·8 per cent.). It combined with chlorine in chloroform solution with evolution of hydrogen chloride; the resulting liquid, after removal of chloroform and standing over sodium hydroxide in a vacuum, slowly deposited crystals, m. p. 61°, which were identical with the trichlorodimethyl*cyclo*hexenone described on p. 1850.

Action of Heat.—The dichlorohexenone was heated gently over a small flame, until evolution of hydrogen chloride ceased and the liquid boiled freely. The dark-coloured product was dissolved in sodium hydroxide, and after acidifying, steam-distilled, when a colourless liquid, which solidified on cooling, was obtained. The product purified by crystallisation from light petroleum (b. p. 40—60°), melted at 82° and was identical with 5-chloro-*o*-3-xylenol (Hinkel, Collins, and Ayling, *loc. cit.*).

Action of Alcoholic Potassium Hydroxide.—The reaction was carried out as described on p. 1850, and 5-chloro-*o*-3-xylenol (*loc. cit.*) obtained.

Action of Sulphuric Acid.—Five grams of the dichlorohexenone were treated exactly as described on p. 1851. The product obtained by steam-distillation slowly solidified on standing and was purified by crystallisation from light petroleum (b. p. 40—60°). The chloroxylenol obtained melted at 98° and was identical with 6-chloro-*o*-4-xylenol, described on p. 1853 (Found: Cl = 22·45 per cent.).

Synthesis of 6-*Chloro*-o-4-*xylenol.*

6-*Chloro*-4-*nitro*-o-*xylene.*—5-Nitro-*o*-3-xylidine (Crossley and Morrell, J., 1911, **99**, 2351) was diazotised at 30° and treated with cuprous chloride in the usual way. The product isolated by distillation with steam crystallised from alcohol in long, silky,

slightly yellow needles, m. p. 101° (Found : Cl = 19·15. Calc., Cl = 19·13 per cent.).

6-*Chloro*-o-4-*xylidine*.—The chloronitroxylene was reduced by stannous chloride in alcohol solution (J., 1923, **123**, 2972). The white solid obtained by distilling the basified liquid with steam crystallised from aqueous alcohol in fine, white needles, m. p. 72° (Found : Cl = 22·81. Calc., Cl = 22·83 per cent.).

6-*Chloro*-o-4-*xylenol*.—6-Chloro-*o*-4-xylidine (3 gms. and 50 c.c. of 40 per cent. sulphuric acid; a sparingly soluble sulphate formed) was diazotised at 0°, the mixture poured into twice its volume of 40 per cent. sulphuric acid and, after standing for one hour, distilled with steam. The solid product crystallised from light petroleum (b. p. 60—80°) in long, silky needles, m. p. 98° (Found : Cl = 22·71. Calc., Cl = 22·68 per cent.).

The *benzoyl* derivative, prepared in the usual way, solidified only after long standing in a cool place, and crystallised from well-cooled alcohol in fine, transparent needles, m. p. 42° (Found : Cl = 13·71. Calc., Cl = 13·62 per cent.).

Trichloro-o-4-*xylenol*, prepared by passing chlorine into a chloroform solution of 6-chloro-*o*-4-xylenol, and removing the solvent, crystallised from dilute alcohol and finally from light petroleum (b. p. 60—80°) in fine needles, m. p. 182·5° (Found : Cl = 47·07. Calc., Cl = 47·22 per cent.).

The *benzoyl* derivative crystallised from alcohol in transparent crystals, m. p. 120° (Found : Cl = 32·17. Calc., Cl = 32·32 per cent.).

Examination of Filtrate A (p. 1850).

On distillation, the liquid yielded two main fractions, (i) 130—148°/13 mm., (ii) 148—160°/13 mm. (Residue = B).

Fraction (i), which became semi-solid on cooling, was repeatedly fractionated, and the transparent crystals which separated on cooling were collected and finally redistilled, when a colourless liquid was obtained, b. p. 129—135°/13 mm., which completely solidified on cooling. The solid, after several crystallisations from light petroleum, melted at 61°, and was identical with the trichlorodimethyl*cyclo*hexenone described on p. 1850. The viscous filtrates from the crystals and also the residue were added to *Fraction* (ii), from which, after frequent distillations, a fraction was obtained, b. p. 145—155°/13 mm. (the residue from this distillation was added to residue B and treated as described on p. 1854). The fraction (b. p. 145—155°/13 mm.), on standing in a cool place, deposited a white, mud-like mass of crystals (8 gms.), which were drained, washed with well-cooled light petroleum, and crystallised from alcohol, 2 : 4 : 5 : 6-*tetrachloro*-1 : 1-*dimethyl*cyclo-Δ^4-*hexen*-3-*one* (XI) separ-

ating in clusters of radiating needles, m. p. 91° (Found : Cl = 53·5. $C_8H_8OCl_4$ requires Cl = 54·19 per cent.).

*Action of Alcoholic Potassium Hydroxide on Tetrachlorodimethyl*cyclo*hexenone.*—The tetrachloro-ketone was treated with alcoholic potassium hydroxide as described on p. 1850. The steam distillate yielded a solid xylenol which, after one crystallisation from light petroleum (b. p. 60—80°), melted at 119—120° (Found : Cl = 35·91. $C_8H_8OCl_2$ requires Cl = 37·18 per cent.).

The *benzoyl* derivative crystallised from alcohol, in which it was almost insoluble in the cold, in feathery, shining plates, m. p. 129° (Found : Cl = 23·0. Calc., Cl = 24·06 per cent.).

*Action of Sulphuric Acid on Tetrachlorodimethyl*cyclo*hexenone.*—The tetrachloro-ketone (3 gms.) was treated exactly as described on p. 1851. The solid xylenol obtained from the steam distillate, after repeated crystallisation from light petroleum, melted at 179°, and no lowering of melting point occurred when it was mixed with either trichloro-*o*-3-xylenol (180°), or trichloro-*o*-4-xylenol (182·5°). Its benzoyl derivative melted unsharply at 112—116°, even after repeated fractional crystallisation from alcohol or light petroleum. The free xylenol and its benzoyl derivative are scarcely changed in m. p. by repeated crystallisation from alcohol, but are slightly less fusible when light petroleum is the solvent. The xylenol appears to be a mixture of the trichloro-derivatives of *o*-3- and *o*-4-xylenols, since the mixed melting point of trichloro-*o*-3- and trichloro-*o*-4-xylenols, and that of their benzoyl derivatives were found to be between 179° and 181° and 112° and 116°, respectively.

Examination of Residue B (p. 1853).—The viscous liquid slowly evolved hydrogen chloride, but without any deposition of crystals, even after standing in a vacuum for several months. The results obtained from the action of sulphuric acid on the liquid were practically identical with those from the tetrachlorodimethyl*cyclo*hexenone (above), pointing to the presence of the latter compound, probably admixed with some still more highly chlorinated compounds which prevent the deposition of the tetrachloro-ketone. The action of heat upon it was therefore investigated. The liquid was gently heated for 1 hour at 130°, and then steam-distilled. The solid xylenol so obtained, after several crystallisations from aqueous alcohol and finally from light petroleum, melted at 182° and yielded a benzoyl derivative, m. p. 120°; the latter was unchanged when the compound was mixed with the trichloro-*o*-4-xylyl benzoate described on p. 1853.

The author desires to express his thanks to the Research Fund Committee of the Chemical Society for a grant which has in part

defrayed the expenses of this investigation, and to Dr. A. W. Crossley for a gift of some organic preparations and for leaving this investigation in his hands.

UNIVERSITY COLLEGE, SWANSEA. [*Received, April 8th*, 1924.]

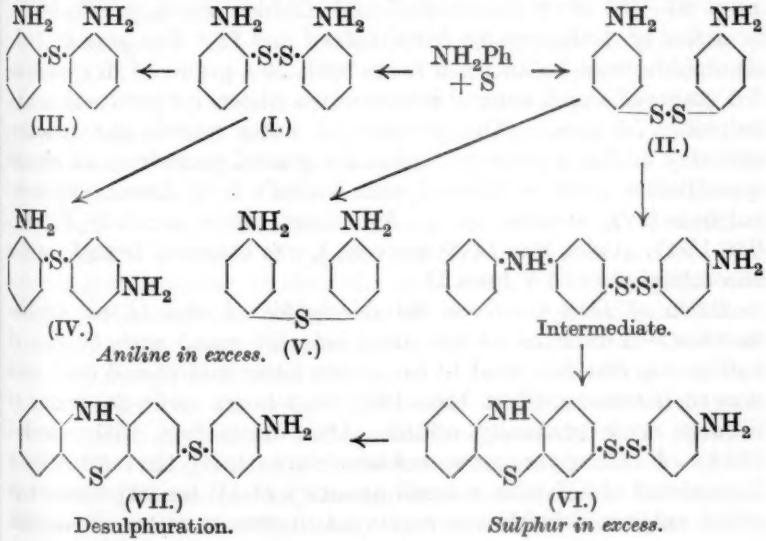
CCXXXIII.—*Direct Sulphuration of Aniline.*

By HERBERT HENRY HODGSON.

COMBINATION between aniline and sulphur appears to commence at 170—180°. 2 : 2′-Diaminodiphenyl disulphide (I) is produced initially, but 4 : 4′-diaminodiphenyl disulphide (II) is formed in increasing quantity as the temperature rises. By prolonged heating, with aniline in excess, the diaminodiphenyl sulphides III, IV, and V are formed, whereas with sulphur in excess the substances VI and VII are produced by diphenylamine condensation followed by further sulphuration and desulphuration.

It has now been shown that Merz and Weith's thioaniline, produced by interaction of sulphur and boiling aniline (*Ber.*, 1871, 4, 384), is a mixture of IV with a small quantity of V, and that their thioaniline formed in presence of lead oxide is the para-substituted sulphide V (compare Nietzki and Bothof, *Ber.*, 1894, **27**, 3261; 1896, **29**, 2774). Hofmann obtained the ortho-substituted disulphide (I) by the direct interaction of sulphur and aniline (*Ber.*, 1894, **27**, 2807).

Lead oxide resembles hydrochloric acid (Hofmann, *loc. cit.*; Hodgson and Dix, J., 1914, **105**, 952) in promoting para-substitution.



Experimental.

The general procedure adopted for the isolation and detection of the reaction products was as follows. After removal of unused aniline (if any) by steam, the product was reduced with alkaline alcoholic sodium sulphide, whereby the disulphides were converted into alkali-soluble mercaptans and thus separated from the sulphides and other insoluble substances. Fractional precipitation by dilute alkali from hydrochloric acid solution, followed by fractional separation from dilute alcohol, then gave either crystallisable material or mixtures, the constituents of which were identified by characteristic colour reactions, determined with the synthetically prepared compounds.

Mixtures of the disulphides were analysed by means of nitrous acid, which converted I into an insoluble diazobenzene sulphide the weight of which was exactly half the theoretical value, and II into a soluble diazo-compound which coupled normally with β-naphthol, giving the theoretical quantity of insoluble azo-naphthol.

The Lead Oxide Experiments of Merz and Weith.—The directions of Merz and Weith were followed. Aniline (1 mol.) and sulphur (1 atom) were heated together for 6 hours at 150—160°. About one-third of the aniline was recovered. The yield of V was very small, but the resinous residue contained a much larger quantity mixed with II, III, and IV. The earlier fractions precipitated by the alkali gave the colour reactions of III and after repeated extraction with boiling water and crystallisation from dilute alcohol yielded a substance, m. p. 87—88° (2 : 2′-diaminodiphenyl sulphide has m. p. 85—86°).

Action of Aniline on the Disulphides I and II.—Ten grams of the disulphide were boiled for 8 hours with 20·4 grams of dry aniline, 7·4 grams of which entered into reaction (theor. for production of a sulphide, 7·5 gms.). The presence of water retards the reaction and may inhibit it entirely. After the general procedure, an almost quantitative yield of Nietzki and Bothof's 2 : 4′-diaminodiphenyl sulphide (IV), needles, m. p. 58°, from dilute alcohol (Found: S = 15·17. Calc., S = 14·86 per cent.), was obtained from I, and a theoretical yield of V from II.

Action of Lead Oxide on the Disulphides I and II in Aniline Solution.—A mixture of the disulphide (24 gms.) with 50 c.c. of aniline was distilled until 10 c.c. of the latter had passed over, and was then maintained at 150—160° for 6 hours while 36 grams of litharge were gradually added. After extraction with alcohol (25 c.c. of aniline were recovered from the extract), the residue from I consisted of III with a small quantity of IV (an experiment in which calcium chloride was employed to remove water of reaction

gave a like result), and the residue from II gave V as almost the sole product.

The Direct Action of Sulphur on Aniline.—In all cases water was removed from the mixture of aniline and sulphur by a preliminary distillation.

(a) *Heating for* 14 *Hours.* Aniline (100 gms.) and sulphur (35 gms.) were gently heated under reflux, the residue after steam distillation was extracted with hot dilute hydrochloric acid, the solution cooled and neutralised, and the precipitate treated by the general procedure. The product consisted mainly of the disulphides I and II in the ratio 2:1, the sulphides IV and V being formed in much smaller quantity.

(b) *Heating for Several Weeks.* Only a green amorphous substance of very high m. p. was obtained, insoluble in acids, sodium sulphide, and the ordinary organic solvents (Found: S = 55 per cent.).

(c) *Heating for* 32 *Hours.* The quantity of the sulphides IV and V increased at the expense of the initially formed disulphides I and II.

(d) *Excess of Aniline* (100 *c.c. of aniline,* 7 *grams of sulphur*). After 14 hours' boiling, a mixture of II, IV, and V was formed, the whole of I having suffered conversion.

After 60 hours' boiling, only monosulphides were present.

(e) *Excess of Sulphur.* In previous work the maximum ratio of sulphur : aniline was 32 : 93. If this ratio is exceeded the nature of the product depends on the temperature and the time of heating: reaction for a short period at a temperature not exceeding 190° (external regulation) produces I mainly; if the reaction mixture be refluxed as long as aniline is present, sulphuration and condensation produce VI and VII.

(i) *Heating for* 16 *hours* (60 *c.c. of aniline* [$\frac{2}{3}$ *mol.*], 32 *grams of sulphur*). The tar remaining after extraction of the reaction product with hydrochloric acid was, when solid, ground, and the green powder (10·5 gms.) digested with carbon disulphide and caustic soda. The residue melted at about 100° [Found: S = 28·83; *M* in phenol = 376. Calc. for $C_{18}H_{14}N_2S_3$ (VI), S = 27·12 per cent.; *M* = 354]. Diazotisation and coupling with β-naphthol indicated the presence of (approximately) one amino-group. The substance was soluble in alcoholic or aqueous sodium sulphide and caustic soda, and the latter solution, by atmospheric oxidation, furnished a product which was only partly soluble in hydrochloric acid; the dissolved portion diazotised and coupled with β-naphthol to give a red azo-compound the colour reactions of which were identical with those of the corresponding compound from II (Found: S = 11·55. Calc. for di-*p*-thiobenzeneazo-β-naphthol, S = 11·46 per cent.). Reduction by zinc and hydrochloric acid, followed by dissolution in caustic alkali and atmospheric oxidation, gave a like

result. The substance therefore contains a dithio-bridge which is split by the two modes of reduction, yielding as one of the products *p*-aminophenyl mercaptan. The tentative formula VI is therefore proposed for this substance.

The deep green acid extract of the original reaction product became very viscous on standing, and, when stirred into dilute alkali, deposited a green solid, which was redissolved in acid and fractionally precipitated by alkali. The yellowish-white base obtained from the earlier fractions was moderately soluble in dilute (1 to 3) hydrochloric acid, and in alcoholic or acid solution gave characteristic colorations with chlorine water, bleaching powder solution, and sodium hypochlorite [Found: S = 20·2; *M* in phenol = 316. Calc. for $C_{18}H_{14}N_2S_2$ (VII), S = 19·87 per cent.; *M* = 322]. A brilliant red pigment is formed on diazotisation and coupling with β-naphthol (Found: S = 13·7 per cent.). If the tentative formula VII be adopted for the base, this pigment would require S = 13·4 per cent.

(ii) *Heating for 48 hours.* The reaction product dissolved almost completely in acid and a slate-blue solid was obtained on making alkaline (Found: S = 20·32 per cent.; *M* in phenol = 317).

The colour reactions and the azo-compound with β-naphthol (Found: S = 12·96 per cent.) were identical with those of the substance VII (above). The substance, being unchanged on treatment with sodium sulphide or zinc and acid, is not a disulphide, and is probably the desulphuration product (VII) of VI. In this connexion, mention may be made of the formation of phenyldiaminophenyl disulphide ($C_6H_5{\cdot}NH{\cdot}C_6H_4{\cdot}S{\cdot}S{\cdot}C_6H_4{\cdot}NH_2$) from aniline, sulphur, and hydrochloric acid (Hofmann, *loc. cit.*).

The author desires to thank Messrs. H. P. K. Robinson and J. H. Wilson for assistance in the very tedious preparative work involved with this investigation.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, April 16th*, 1924.]

CCXXXIV.—*The Ignition of Gases. Part III. Ignition by the Impulsive Electrical Discharge. Mixtures of the Paraffins with Air.*

By RICHARD VERNON WHEELER.

IN Part I of this research (J., 1920, **117**, 903) experimental data and theoretical considerations were advanced to show that the general ignition, or otherwise, of an inflammable mixture of methane

and air by a momentary but intense source of heat, such as the secondary discharge, is dependent in a considerable degree upon the rapidity with which flame spreads through a sufficient volume of the mixture. That is to say, on the initial speed of propagation of flame in the mixture. If this view is correct, there should be a fairly close correspondence between the initial speeds of flame in other mixtures and their ignitibility by electric sparks as measured by some standard means, the closeness of the correspondence depending upon the degree to which other factors, such, for example, as "ignition-temperature," affect ignitibility by an intense source of heat of momentary duration.

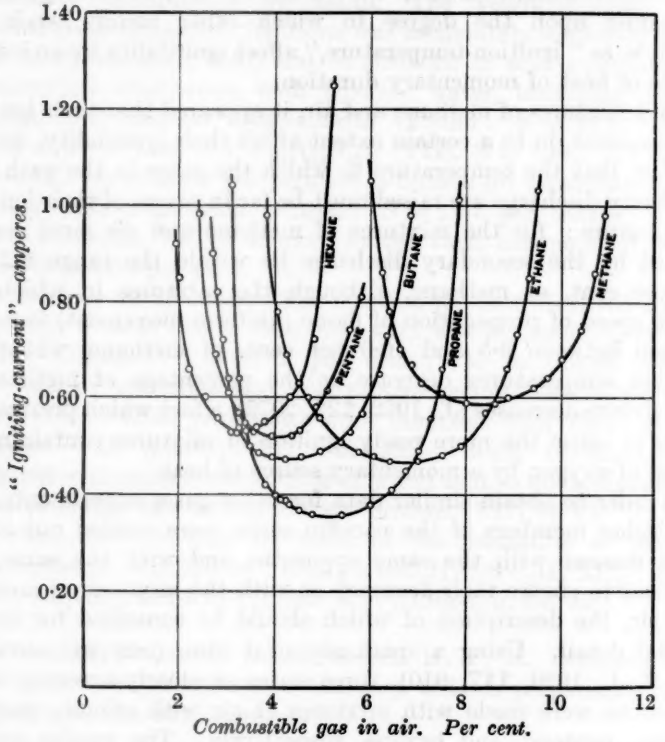
With mixtures of methane and air, it appeared that their ignition temperatures do to a certain extent affect their ignitibility, despite the fact that the temperature to which the gases in the path of a secondary discharge are raised must be far in excess of their ignition temperature: for the mixtures of methane and air most readily ignited by the secondary discharge lie within the range 8·2 and 8·5 per cent. of methane, although the mixtures in which the initial speed of propagation of flame (uniform movement) is fastest contain between 9·5 and 10·0 per cent. of methane, whilst the ignition temperatures decrease as the percentage of methane in the mixture decreases (J., 1922, **121**, 2079), a fact which presumably tends to cause the more ready ignition of mixtures containing an excess of oxygen by a momentary source of heat.

In order to obtain similar data for other gases experiments with the higher members of the paraffin series were carried out in the same manner with the same apparatus and with the same precautions to ensure their accuracy as with the mixtures of methane and air, the description of which should be consulted for experimental detail. Using a spark-gap of 1 mm. (compare curve A, Fig. 3, J., 1920, **117**, 910), three series of closely-agreeing determinations were made with mixtures of air with ethane, propane, butane, pentane, and hexane, respectively. The results are expressed in Fig. 1 as graphs relating percentages of inflammable gas with "igniting-currents," that is to say, the currents in the primary circuit of the induction-coil used which, when broken at a constant rate, induced at a fixed spark-gap secondary discharges that were just capable of igniting the mixtures. It has been found that when, as in these experiments, the spark-gap is between sharply-pointed electrodes, the intensity of the capacity component of the spark is directly proportional to the current broken in the primary circuit.

All the curves have the same general character and are well-defined and perfectly smooth; but, as so often happens with the

first member of a homologous series, methane stands apart from the other gases, inasmuch as the mixture with air that requires the lowest "igniting-current" contains an excess of oxygen, whereas with all the other hydrocarbons the most readily ignitible mixture contains an excess of combustible gas. The significant figures, together with other data bearing on the subject, are recorded in Table I.

FIG. 1.



Inasmuch as, with each of the higher paraffins, the mixture with air in which the speed of uniform movement of flame is fastest contains an excess of combustible gas, the values for the mixtures most readily ignited by the secondary discharge are in general conformity with the suggestion that the initial speed of flame in a mixture, away from a point source of heat of momentary duration, is the dominant factor in determining what the intensity of such a source of heat must be to cause the general ignition of the mixture.

The relationship that exists between the intensity of spark required to cause the general ignition of a mixture and the speed

TABLE I.

Mixtures of the Paraffins with Air.

Combustible gas.	Limits of * inflammability. Lower. Per cent.	Limits of * inflammability. Upper. Per cent.	Mixture in which speed of uniform movement of flame is fastest.† Per cent.	Mixture for complete combustion. Per cent.	Mixture most readily ignited by secondary discharge. Per cent.
Methane	5·60	14·80	9·65	9·45	8·3
Ethane	3·10	10·70	6·05	5·64	6·7
n-Propane	2·17	7·35	4·45	4·02	5·1
n-Butane	1·65	5·70	3·65	3·13	4·2
n-Pentane	1·35	4·50	2·90	2·56	4·0
n-Hexane	—	—	—	2·15	3·2

* Central ignition in 3-litre globe (Burgess and Wheeler, J., 1911, **99**, 2013).
† In horizontal brass tube 5 cm. diam. (Mason, J., 1923, **123**, 210).

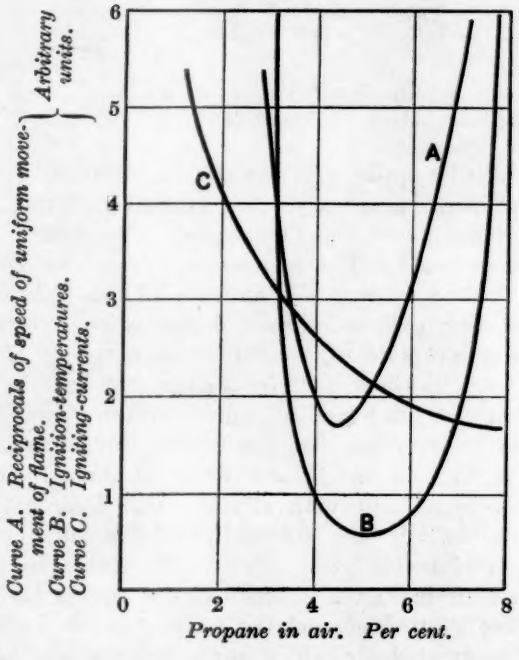
of flame in it will be apparent if comparison is made between the igniting-current percentage curves for methane, ethane, propane, butane, and pentane and the flame-speed percentage curves for the same gases recorded in Fig. 2 of Mason's paper (*loc. cit.*). This the reader is invited to do. For any one of the paraffin hydrocarbons the relative igniting-currents of the various mixtures with air are inversely proportional to the relative speeds of uniform movement of flame in them, save for a slight but definite displacement of the range of most readily ignited mixtures away from the range in which the speed of flame is fastest. With methane this displacement is towards the " lower-limit " (mixtures containing an excess of oxygen), but with all the other hydrocarbons the displacement is towards the " upper-limit " (mixtures containing an excess of combustible gas). This is illustrated for mixtures of propane and air in Fig. 2, where curve A shows the percentages of propane plotted against the reciprocals of the speeds of uniform movement of flame, whilst curve B is the igniting-current curve.

When discussing the results obtained with mixtures of methane and air, the explanation offered of the displacement of the range of mixtures having the lowest igniting-currents, towards the lower-limit, was that the lower ignition-temperatures of the mixtures containing an excess of oxygen cause them to be rather more readily ignited by an intense source of heat of short duration. A corresponding explanation can be given with respect to mixtures of propane and air, where the " displacement " towards the upper limit can be accounted for by the fact that the relative ignition-temperatures of mixtures of propane and air decrease as the

percentage of combustible gas increases, as shown in curve C, Fig. 2.

Details of the determination of the relative ignition-temperatures of mixtures of propane and air are given in Part IV (this vol., p. 1869) of this research, together with corresponding values for mixtures of ethane, butane, and pentane, respectively, with air. With each of these gases, as with propane, the ignition-temperature decreases as the percentage of combustible gas is increased. Methane stands alone of the series of hydrocarbons with respect to the high ignition-

FIG. 2.



temperatures of mixtures with air containing an excess of combustible gas, just as it stands alone of the series with respect to the sense of the displacement of the range of mixtures most readily ignited by the secondary discharge. The suggestion made regarding the *rationale* of ignition of mixtures of methane and air by the secondary discharge thus receives strong support from the results obtained with other paraffin hydrocarbons.

When we come to compare one paraffin with another, however, there is seen to be a departure from the general principle that the ease of ignition of an inflammable mixture by a momentary source of heat is closely related with the initial speed of flame in

that mixture. In Table II are recorded the relative values of the "igniting-currents" for the most readily ignited mixture and the "maximum-speed" mixture * of each hydrocarbon with air, together with the relative values for the speed of uniform movement of flame in these mixtures and for their ignition temperatures.

TABLE II.

Mixtures of the Paraffins with Air.

	Relative igniting currents (amp.).		Relative speeds of flame (cm. per sec.).[1]		Relative ignition temp.[2]	
Combustible gas.	Most readily ignited mixture.	Maximum-speed mixture.	Most readily ignited mixture.	Maximum-speed mixture.	Most readily ignited mixture. (By secondary discharge.)	Maximum-speed mixture.
Methane ...	0·59	0·64	70	91	692°	700°
Ethane ...	0·47	0·48	120	127	544	548
Propane ...	0·36	0·37	100	114	522	528
Butane ...	0·48	0·49	80	113	508	515
Pentane ...	0·52	0·72	50	115	502	518

[1] Mason (*loc. cit.*). [2] See Part IV of this research.

It will be understood that none of the values in Table II has any absolute significance, nor is it possible to gauge the comparative significance of, for example, 10° difference in "ignition temperature" and 0·1 amp. difference in "igniting-current." The values in each group of determinations are, however, directly comparable one with another and are correct within small margins of experimental error.†

The sequence into which the gases fall with respect to the maximum speed of uniform movement of flame in their mixtures with air is, according to Mason: (1) ethane, (2) propane, butane, and pentane, (3) methane, whilst according to Payman, whose determinations were made with a glass tube 2·5 cm. in diameter, there is not much difference between the maximum speeds obtained with any of the gases except methane, with which the value is markedly lower than with the others (J., 1919, **115**, 1446). The sequence with respect to the igniting-currents of the most readily ignited mixtures with air is: (1) propane, (2) ethane and butane, (3) pentane, and (4) methane.

This sequence is clearly displayed by the curves in Fig. 1, from which it will be seen that propane yields mixtures that are decidedly

* The term "maximum-speed" mixture is used to denote that mixture in which the speed of uniform movement of flame is greatest.

† The probable experimental error is: for igniting-current, ±0·005 amp.; for speed of flame, ±1 cm. per second; and for ignition-temperature, ±1°.

the most readily ignited of any. There is no outstanding reason for this according to the arguments herein advanced (which would rather accord to ethane the position that propane occupies), although it will be noticed (Table II) that the most readily ignited mixture of propane and air has both a low ignition-temperature (lower than that of the corresponding mixture of ethane and air) and a high speed of propagation of flame (higher than that of the corresponding mixture of butane and air).

A better test of the soundness of the argument that ignitibility by a momentary source of heat is related to speed of propagation of flame, as applied to different inflammable gases, than can be given by the members of the paraffin series of hydrocarbons which all yield mixtures with air in which the speed of flame is slow, would be afforded by a gas of which mixtures with air propagate flame at a considerably higher speed. Such a gas is hydrogen. The speed of uniform movement of flame in the "maximum-speed" mixture of hydrogen and air is about six times as great as with any of the paraffins. On attempting to determine the "igniting-currents" of mixtures of hydrogen and air under conditions directly comparable with those employed for the paraffins as recorded in Fig. 1, the difficulty presented itself that for all save mixtures near the limits of inflammability a spark-gap of 1 mm. was too great, since any spark that could jump a gap of this width would also ignite the mixture. To determine the relative "igniting-currents" for mixtures of hydrogen and air for comparison with the paraffins, a spark-gap of less than 0·25 mm. had to be employed, when it was found that the igniting-current for the most readily ignited mixtures of hydrogen and air (containing between 26 and 28 per cent. of hydrogen) was 0·36 ampere, whilst with the same spark-gap the igniting-current for the most readily ignited mixture of ethane and air (containing 6·7 per cent. of ethane) was 3·4 amperes. These values should be compared with those for the relative speeds of propagation of flame in the mixtures, which are: for hydrogen and air, 400 cm. per second; and for ethane and air, 80 cm. per second.

A factor that might perhaps influence the igniting-power of a secondary discharge is the insulating power of the medium through which it passes. Over the range of mixtures with air of any one of the gases experimented with, this is nearly constant; but as between one inflammable gas and another there are appreciable differences, as shown by some determinations made for me by Mr. R. Wright (see J., 1918, **113**, 79). A measure of the insulating power is given by the spark-lengths under standard conditions in the pure gases at a temperature of 138°, as follows:

TABLE III.

Spark-lengths in the Paraffins.

Gas.	Spark-length (mm.).	Gas.	Spark-length (mm.).
Methane	31	*n*-Butane	16
Ethane	25	*n*-Pentane	14
Propane	20	*iso*Pentane	10

From these results it appears that increase of molecular weight in the series of paraffins is attended by increase in insulating power such as would cause the voltage of secondary discharge obtained on breaking a given current in the primary circuit to attain higher peak values at a given spark-gap as the series is ascended, but the increase is fairly regular and offers no explanation of the fact that the most readily ignited mixtures of any of the paraffins with air are those of propane. It is doubtful, however, whether the differences observable in the insulating power of the pure inflammable gases are sufficient to produce any noticeable effect when the medium at the spark-gap contains only a small percentage of inflammable gas. This point was tested by making parallel experiments with a number of mixtures of *n*-pentane and *iso*pentane respectively with air. Pure *iso*pentane offers considerably higher resistance to the passage of an electric discharge than does *n*-pentane (see Table III). The results are recorded in Table IV.

TABLE IV.

Comparison of "Igniting-currents" of n-*Pentane and* iso*Pentane respectively mixed with Air.*

Per cent. in air.		Igniting-current. Ampere.	
n-Pentane.	*iso*Pentane.	*n*-Pentane.	*iso*Pentane.
3·00	2·97	0·61	0·61
3·90	3·87	0·53	0·53
4·30	4·34	0·53	0·54
5·21	5·20	0·63	0·63

No difference in the ignitibility of corresponding mixtures could be detected between the two isomerides and it can be concluded that any difference there may be between the insulating powers of the mixtures does not appreciably affect the igniting-powers of secondary discharge passing in them.

When considering the results of these experiments, the significance of the phrase "the general ignition of the mixture" which has been used in describing them must be appreciated. The experiments were carried out in a spherical glass vessel of about 75 c.c. capacity, the 1 mm. spark-gap being formed horizontally at the centre of the vessel between sharply pointed wires of platinum

coated with glass to within 1 mm. of their ends. A spark-gap of this description, formed between electrodes of but small mass and having but little cooling surface, presents very little obstacle in the way of flame travelling from it (in this connexion, see Morgan, *Phil. Mag.*, 1923, [vi], **45**, 968). Nevertheless, some cooling by the electrodes must occur. Evidence of such cooling is no doubt given by the fact, referred to in Part I of these researches (*q.v.*), that with any given inflammable mixture the passage of a discharge of slightly less intensity than that which causes flame to travel throughout the explosion-vessel produces transient tongues of flame above and below the spark-gap.

The character of these tongues of flame, which are observed with all the hydrocarbons (most markedly with mixtures of ethane and air, in which they are of an intense blue colour), emphasises the necessity that must exist for a certain minimum volume, even of the most explosive mixture, to be burnt if the continued progress of flame throughout the mixture is to result; for their length in a given mixture gradually increases as the intensity of the discharge is increased, being barely measurable when they are first observed (as a faint blue haze around the spark-gap) and reaching as much as 2 or 3 mm. when the discharge is almost capable of causing general ignition of the mixture.

If the source of heat used in an attempt to effect the ignition of a given mixture is withdrawn almost as soon as it is introduced, as when a secondary discharge at a fixed spark-gap of constant length is employed (the duration of the capacity component of the secondary discharge is less than 0·00005 second), the combustion of the minimum volume of gas necessary to enable flame to spread throughout the mixture is dependent entirely upon the distance to which flame is suddenly projected as the spark passes. For a given mixture in which the initial speed of flame normally has a certain low value the distance to which flame is projected away from a spark-gap is dependent upon the intensity of the spark, which imparts an impetus to the flame of increasing magnitude as its intensity increases. Whilst with a spark of a given low intensity the distances to which flame is projected in different mixtures vary with the normal initial speed of flame in those mixtures, so that a mixture in which the initial speed of flame is rapid will be "ignited" by such a spark and one in which the initial speed of flame is slow will not be ignited.

Strictly speaking, no doubt, the "ignition" of a mixture by an electric spark occurs when a transient tongue of flame appears at the spark-gap, and it might be profitable to attempt to determine the intensity of spark required to produce a tongue of flame of

given length, or by such means to obtain some measure of the minimum volume of different mixtures that must be burnt before flame can be propagated through them.

The intensity of spark with which flame at the spark-gap can be detected with certainty is, however, ill-defined. It can be assumed that any spark that passes causes combination of gases in its path—causes "ignition" of part of the mixture—and it is doubtful whether any useful purpose would be served by recording when this local "ignition" becomes apparent.

The study of the "ignition" of gases by electric sparks—ignition by a momentary source of heat—should be regarded, therefore, more as a study of the propagation of flame than of its initiation. On the other hand, we are not concerned in this study with the *continued* propagation of flame, and it will be seen that in several instances the "igniting-currents" for mixtures that lie outside the limits of inflammability at atmospheric temperature and pressure are recorded. Such mixtures allow flame to travel in them for a short distance and if the vessel that contains them is small the "cap" of flame produced around a source of heat within the vessel may fill it (see J., 1920, **117**, 913).

I have had the advantage of discussing this work with Dr. S. C. Lind, Chief Chemist of the United States Bureau of Mines, whose researches on gaseous reactions under the influence of α-particles are well-known. Dr. Lind pointed out a possible explanation of the results which appeared to me most suggestive and which, at my request, he has embodied in an addendum to this paper.

Safety in Mines Research Board,
Experimental Station, Sheffield. [*Received, May 13th*, 1924.]

*Addendum.**

By Samuel Colville Lind.

Through the courtesy extended as a result of the co-operation of the Safety in Mines Research Board of Great Britain with the United States Bureau of Mines, I have had the privilege of reading Professor Wheeler's paper in manuscript and of discussing it with him.

I have been struck by the result that the most readily ignitible mixture of methane and air (8·3 per cent. methane) contains a higher percentage of air than do the mixtures either for complete combustion or for fastest flame propagation, whilst for mixtures of all

* Published by permission of the Director of the United States Bureau of Mines, Department of the Interior.

the higher paraffins with air the reverse is true, *i.e.*, a mixture poorer in air than that for complete combustion or most rapid flame propagation is the most easily ignited by a momentary source of heat. This apparent anomaly suggests that absolute density of the mixture may be the controlling factor. In seeking to explain this, I have been impressed with the similarity of the case to that of the velocity of interaction of hydrogen and oxygen under the influence of α-particles, where departure from the equivalent mixture in the direction of excess hydrogen (lower density or "stopping power") lowers the velocity, whilst excess of oxygen (higher density and stopping power) increases the velocity (see *J. Amer. Chem. Soc.*, 1919, **41**, 542). Professor Wheeler reminds me that this exactly parallels what Dixon and Crofts found (J., 1914, **105**, 2036) for the ignition-temperatures of mixtures of hydrogen and oxygen; excess oxygen lowered the temperature whilst excess hydrogen raised it, as one would expect if density were the controlling factor. Strong confirmation of this view is given by the fact, referred to in the present paper, that with the paraffins (methane excepted) the lowest ignition-temperature is obtained with a mixture containing excess of the combustible gas.

In gaseous reactions brought about by the action of α-particles, the specific ionisation of the mixtures as controlled by their relative stopping powers affords a satisfactory explanation of the observations. It is not proposed to attempt to translate an explanation of this kind too literally into terms of flame propagation, nor is it necessary to do so. If it is permissible to assume flame propagation to be due to the radiation of energy in some form which is subject to a non-selective absorption roughly proportional to the density of the gaseous medium, Wheeler's and Dixon and Crofts' observations receive a direct explanation.

The α-particle experiments also make it clear that excess of one of the components of a reaction mixture is not to be regarded as a diluent in slow reactions, no matter how far one departs in either direction from the equivalent mixture. Of course, in flame reactions, for obvious reasons, one may not depart very far without the excess becoming virtually a diluent, but it is significant to note that the departure (within the narrow limits allowable) is in the direction that would be predicted from the "stopping power" principle.

One other difference should be pointed out. In the α-particle experiments each particle traverses the entire gas space from its point of origin to the wall. Presumably the radiation causing ignition is not very penetrating and may be regarded as being absorbed within a relatively small radius from its point of origin;

therefore, lowering the density of the gas mixture will not diminish the total energy absorption, but will extend it over a larger sphere and hence diminish the reaction concentration, which is unfavourable to flame propagation. This may be illustrated by considering the case of a thin α-ray bulb mounted at the centre of the reaction sphere to replace Professor Wheeler's spark ignition. If it were possible, at some pressure of the gases to be ignited, to introduce suddenly a sufficient quantity of radon (RaEM) into the bulb to cause ignition,* the composition of the critical mixture would undoubtedly be controlled by the laws of "stopping power" for α-rays.

In the case of a methane–oxygen mixture the values of specific ionisation of methane (1·10) and of oxygen (1·09) are practically identical and do not indicate that there would be by ionisation any difference of efficiency for α-radiation in mixtures of varying proportions. On the other hand, the "stopping power" for α-rays, 0·86 for methane and 1·064 for oxygen, would indicate a difference in the direction which would explain Professor Wheeler's results. It would be of interest to compare experimentally the relative rates of reaction in various mixtures of oxygen and methane under α-radiation.

WASHINGTON.
March, 1924.

CCXXXV.—*The Ignition of Gases. Part IV. Ignition by a Heated Surface. Mixtures of the Paraffins with Air.*

By WALTER MASON and RICHARD VERNON WHEELER.

IT has been explained in Part II of this research (J., 1922, **121**, 2079) that the ignition of a given inflammable mixture by a heated surface depends not only on the temperature of that surface but on the length of time during which the mixture is exposed to it. In general, ignition by heated surfaces is so dependent upon the experimental method used that records of "ignition-temperatures" of different mixtures obtained by these means have only relative significance. For example, the material of the surface, its texture, and the ratio that its area bears to the volume of an inflammable mixture exposed to it, all affect considerably the temperature to which it has to be raised in order to ignite that mixture; whilst, so far as the mixture itself is concerned, the manner in which it

* Scheuer (*Compt. rend.*, 1914, **159**, 423) claims to have caused ignition in one instance by suddenly mixing radon and electrolytic hydrogen and oxygen.

is presented to the heated surface (whether in a quiescent or a turbulent state) will—because the duration of contact is so important—determine its ignition or otherwise at a given temperature.

Nevertheless, provided that no alteration of indeterminate effect is made in the conditions of experiment, a heated surface can usefully be employed to measure the relative ignitibilities of different mixtures, or to obtain information regarding the times of contact necessary to ensure ignition at different temperatures.

This was the information sought in the present research. Two main groups of experiments were made: in the one, relative ignition-temperatures of different mixtures of the paraffins with air were determined, whilst in the other, the "lags" on ignition (see J., 1922, **121**, 2085) at temperatures higher than these "ignition-temperatures" were measured.

Relative Ignition Temperatures.

The mixture to be experimented with was rapidly admitted to an evacuated cylinder of quartz (of 85 c.c. capacity) in sufficient volume to be at atmospheric pressure when it had attained the temperature of the walls of the vessel. The lowest temperature to which the walls had to be previously heated in order that the mixture should eventually ignite was regarded as the "ignition-temperature" of the mixture relative to that of other mixtures admitted to the same vessel in the same manner.

The results of similar experiments previously recorded for mixtures of methane and air (*loc. cit.*, p. 2081) were obtained with a quartz vessel that suffered damage during later work, and fresh determinations with a new vessel had to be made for comparative purposes. These are recorded in Table I together with the corresponding values for mixtures of ethane, propane, butane, and pentane with air.

It should be borne in mind that the temperatures recorded in Table I are the lowest temperatures at which, under the conditions of the experiments, the various mixtures could be caused to inflame however long they remained in contact with the heated surface. In many instances, the interval that elapsed between the admission of the mixture to the heated vessel and the appearance of flame was prolonged. In carrying out a series of experiments with a particular mixture it was usual to work downwards to the "relative ignition-temperature" from a higher temperature by intervals of at first 5° and later 1°, and the differences in the "lags" as the lowest temperature at which ignition could be obtained was approached were most marked. For example, the lag on ignition of a mixture containing 6·0 per cent. of methane was 10 seconds

TABLE I.

Relative Ignition Temperatures.

Methane.							
Per cent. in air	2·45	4·05	6·00	8·00	10·15	11·40	12·80
Relative ignition temp.	690°	684°	685°	692°	703°	711°	720°
Ethane.							
Per cent. in air	1·90	2·80	4·05	4·85	5·70	8·15	10·60
Relative ignition temp.	594°	571°	560°	555°	550°	540°	534°
Propane.							
Per cent. in air	1·25	2·50	3·05	4·90	6·50	7·85	
Relative ignition temp.	588°	552°	544°	525°	516°	514°	
Butane.							
Per cent. in air	1·25	2·00	2·60	3·65	4·85	7·65	
Relative ignition temp.	569°	545°	531°	515°	502°	489°	
Pentane.							
Per cent. in air	1·50	2·15	2·75	3·75	5·30	7·65	
Relative ignition temp.	548°	532°	520°	502°	486°	476°	

when the temperature of the heated vessel was 686° and 11·7 seconds when it was 685° (the " relative ignition temperature," see Table I).

In general, the duration of the lag on ignition at their relative ignition temperatures for all mixtures of methane and air containing an excess of oxygen was between 10 and 16 seconds, whilst it decreased rapidly as the methane-content was increased beyond 9·45 per cent., the value with a mixture containing 12·80 per cent. of methane being 6·6 seconds (at 720°).

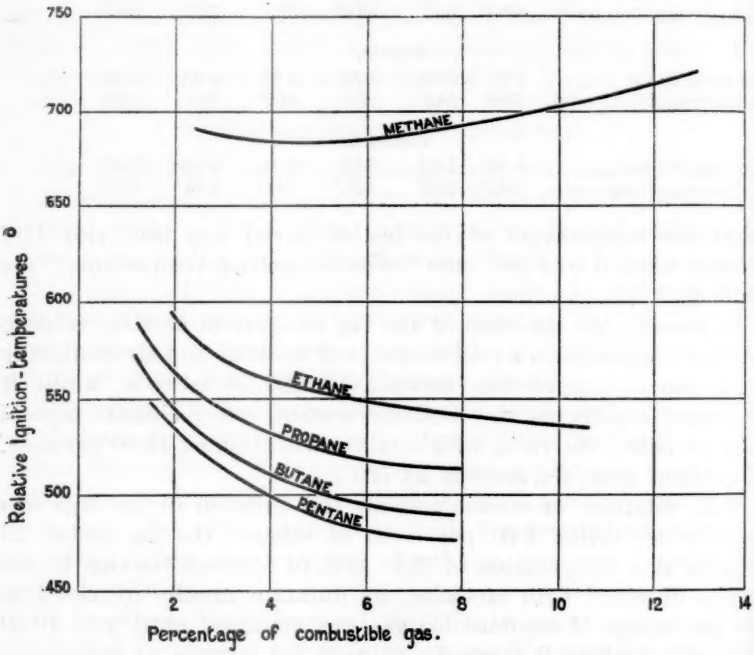
With mixtures of ethane and air the duration of the lags was remarkable. With 1·90 per cent. of ethane, the lag lasted 28 seconds at a temperature of 594° and, in contradistinction to the results obtained with methane, its duration rapidly increased as the percentage of combustible gas was increased until with 10·60 per cent. of ethane it reached a value of 144 seconds (at 534°).

With mixtures of propane and air the values for the " lags " increased gradually from 20 seconds (for a mixture containing 1·25 per cent. of propane at 588°) to 56 seconds (for a mixture containing 7·85 per cent. of propane at 514°). With butane, the lag on ignition of all the mixtures lasted between 22 and 25 seconds; and with pentane, the lags for mixtures containing between 1·50 and 3·75 per cent. lasted about 15 seconds, for a 5·30 per cent. mixture, 9 seconds (at 486°) and for a 7·65 per cent. mixture, 5 seconds (at 476°).

In each instance the records showed but a slight increase in pressure within the reaction-vessel during the period of lag, whilst

the production of flame, even when, as with ethane, it occurred after an interval of one or two minutes, was accompanied by a sharp pressure rise. The period of lag, during which the rate of reaction between oxygen and the combustible gas is increasing until it becomes rapid enough to produce flame, must, however, allow of a certain amount of reaction, so that the mixture which ultimately inflames may not be of the same composition as that originally admitted to the heated vessel. With mixtures of methane and air, any change that can take place is not great (according to

FIG. 1.



the results of analysis of the gases removed from the reaction-vessel half-way through the period of lag), even if it is assumed that the products of the initial slow reaction at and near the walls of the vessel have time to diffuse throughout the whole of the remainder of the mixture; but with some of the mixtures of ethane and air containing an excess of ethane it is conceivable that ignition ultimately occurred only because of the liberation of hydrogen during one of the stages of slow combustion. There was no evidence that, with any of the hydrocarbons, thermal decomposition took place under the conditions of the experiments.

As regards the ignitibility of the paraffins, as measured by their

relative ignition-temperatures, the mixtures of methane and air are appreciably the most difficult to ignite, whilst the others become easier to ignite as the series is ascended. The most striking feature of the results is best displayed by curves (Fig. 1), in which, for each hydrocarbon, relative ignition-temperatures are plotted against percentages of combustible gas in admixture with air. It will be seen that whereas with methane the lowest ignition-temperatures are obtained when there is excess of oxygen, although over a wide range the variation (8° between 2·5 and 8·0 per cent. of methane) is not great, with all the other hydrocarbons there is a gradual diminution in the ignition-temperature as the proportion of the combustible gas is increased.

We regard as the most satisfactory theory to account for these facts that advanced by Lind in an addendum to Part III of these researches (this vol., p. 1867): namely, that the rate of reaction between a combustible gas and oxygen increases with the concentration of whichever has the greater "stopping-power" for radiant energy such as will "activate" it; and that this stopping-power depends on the density of the gas just as does the stopping-power for α-rays, for which the following values, relative to air, are given by Bragg ("Studies in Radioactivity," p. 49. London, 1912):

Gas.	*Stopping-power for* Ra-*C.*
Oxygen	1·067
Methane	0·860
Ethane	1·519
Pentane	3·544

The Pre-flame Period.

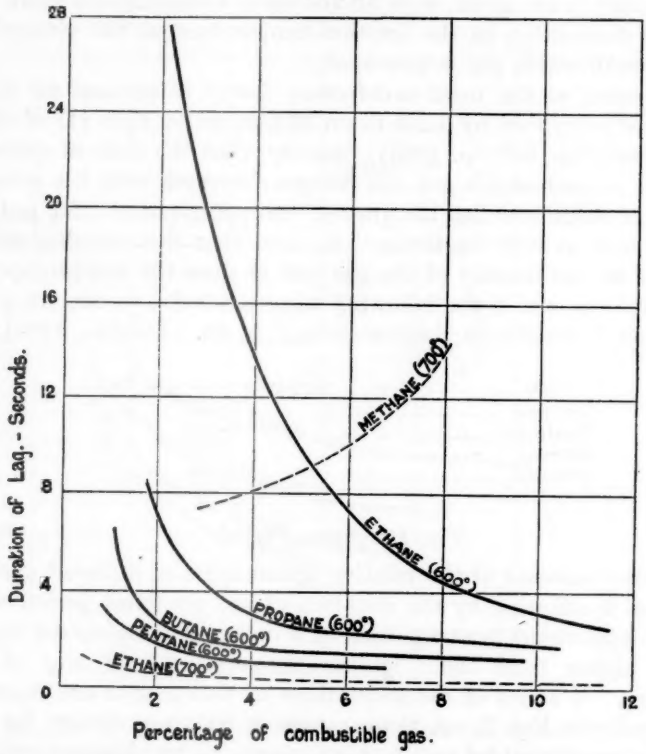
Another measure of the relative ignitibilities of different gaseous mixtures is afforded by the duration of the pre-flame period when the reaction-vessel is maintained at a constant temperature appreciably higher than the "ignition-temperature" of any of the mixtures. A series of determinations of this nature are recorded graphically in Fig. 2. A temperature of 600° was chosen for this series, since it enabled satisfactory records to be obtained with all the gases (except methane), although with mixtures rich in pentane, the ignition-temperatures of which were over 100° less than the experimental temperature, the lags lasted less than one second.

Just as when measured by the standard of "ignition-temperature," the mixtures containing an excess of combustible gas, with all the higher paraffins, are found to be the more readily ignitible inasmuch as they require to be exposed to a heated surface at a temperature of 600° during a shorter time in order that flame shall appear. No records could be obtained for methane at 600°, since

the ignition-temperature of all its mixtures with air is well above that temperature, but a series of determinations at 700° is reproduced as a curve in dotted line in Fig. 2 for comparison as to general character; whilst direct comparison can be made with the curve for ethane–air mixtures at 700° shown at the foot of Fig. 2.

Taking as the basis of comparison the lower-limit mixtures of the different gases with air at atmospheric temperature and pressure, that is to say, the mixtures containing the least quantity of com-

FIG. 2.



bustible gas that will admit of continued propagation of flame away from the source of ignition, these experiments show that the lower-limit mixture of methane (5·8 per cent. methane) would have to remain during 9·8 seconds, whilst that of ethane (3·3 per cent. ethane) during less than half a second, in contact with the same source of heat at a temperature of 700° in order that it might ignite. Comparing the higher paraffins amongst themselves, the relative figures at a temperature of 600° are: ethane, 17·5 seconds; propane (2·4 per cent. propane), 5·6 seconds; butane (1·9 per cent.

butane), 3·2 seconds; and pentane (1·6 per cent. pentane), 2·2 seconds.*

When the source of heat to which the different mixtures are exposed is at a considerably higher temperature than their ignition-temperatures, say 1000° or more, the "lags" become exceedingly short, but differences in the lags as between one gas and another are still measurable, and to these differences must be ascribed, in part, their varying sensitiveness to ignition by an intense source of heat of short duration.

Experimental.

The apparatus used, and the manner of conducting the experiments, have been fully described in J., 1922, **121**, 2089. The following determinations of "lags" on ignition at different temperatures, additional to those recorded graphically in Fig. 2, are of interest.

Temperature 650°.				*Temperature* 550°.			
Ethane–Air Mixtures.		*Propane–Air Mixtures.*		*Butane–Air Mixtures.*		*Pentane–Air Mixtures.*	
Ethane per cent.	Lag (secs.).	Propane per cent.	Lag (secs.).	Butane per cent.	Lag (secs.).	Pentane per cent.	Lag (secs.).
12·25	0·75	9·10	0·88	9·75	2·99	8·80	1·55
8·65	0·89	4·55	1·06	6·80	4·43	5·35	2·40
4·00	1·37	1·45	1·71	5·40	5·95	2·35	6·67
1·80	2·41	0·95	2·24	4·15	12·93	1·80	11·37
0·85	6·05			2·75	20·45		

This work has been continued to determine the lags on ignition when the heated surface is at a temperature considerably above the ignition-temperature of the mixtures.

Experimental Station,
Eskmeals, Cumberland. [*Received, July 12th*, 1924.]

CCXXXVI.—*Investigations of the Chromates of Thorium and the Rare Earths. Part II. The Chromates of Lanthanum, Praseodymium, Neodymium, and Samarium.*

By Hubert Thomas Stanley Britton.

Of the many methods which have been employed for the separation of the rare earths, that by the fractional precipitation of the chromates appears to offer advantages not yet fully realised. Thus

* The values of the lower-limit mixtures are all for horizontal propagation of flame in a glass tube 2·5 cm. in diameter.

Böhm (*Z. angew. Chem.*, 1902, **15**, 1282) has shown that a preliminary application of the chromate method is advantageous in the separation of praseodymium from neodymium, and other workers, Moissan and Etard (*Compt. rend.*, 1896, **122**, 573), Muthmann and Böhm (*Ber.*, 1900, **33**, 42), Dennis and Dales (*J. Amer. Chem. Soc.*, 1902, **24**, 401), Egan and Balke (*ibid.*, 1913, **35**, 365), Meyer and Wuorinen (*Z. anorg. Chem.*, 1913, **80**, 7), and Holden and James (*J. Amer. Chem. Soc.*, 1914, **36**, 638), have applied the method to the yttrium earths with success. The work described here was undertaken to enlarge the very scanty information hitherto available on the properties of the individual chromates concerned in these separations.

Experimental.

The general method of preparing these chromates was that used by Böhm for their separation. About 2 grams of the rare earth were dissolved in the minimum amount of a concentrated chromic acid solution and the resulting solution was diluted to about ½ litre. The precipitation of the chromates was effected by the gradual addition, with stirring, of *M*/10-potassium chromate. When the amount of chromic acid used was kept sufficiently low, the quantity of potassium chromate required was small, thereby causing the simple chromate alone to be precipitated, but if too great a quantity of acid had been employed a correspondingly large amount of precipitant was necessary and this often caused the precipitation of double chromates together with varying amounts of simple chromates. An explanation of the precipitating action of potassium chromate is forthcoming from a consideration of the ionisation of chromic acid solutions (*vide* Britton, this vol., p. 1580). As the precipitation of a difficultly soluble chromate is regulated by its solubility product, the main factor involved is the concentration of CrO_4'' ions. The concentration of chromate-ions is negligibly small in free acid solutions, but becomes appreciably greater when the inhibiting ion—the first hydrion—has been replaced. This condition is reached when the amount of potassium chromate added and the chromic acid initially present are in equimolecular proportion. From this point, on further addition of potassium chromate the concentration of chromate ions gradually increases, so that if the four earths were present the solubility products of their respective chromates would in turn be exceeded.

The rare earths used in this work were pure as far as could be ascertained from their properties and their equivalent weights. The following chromates have been isolated, and were analysed in a manner similar to that employed for thorium chromate (Britton,

J., 1923, **123**, 1429); the theoretical percentages are given in brackets:

Lanthanum chromate, $La_2(CrO_4)_3,8H_2O$.

$La_2O_3 = 42{\cdot}29$ (42·34); $CrO_3 = 39{\cdot}07$ (38·96).

Praseodymium chromate, $Pr_2(CrO_4)_3,8H_2O$.

$Pr_6O_{11} = 43{\cdot}85$ (43·95); $CrO_3 = 38{\cdot}90$ (38·80).

It has been shown recently by Brinton and Pagel (*J. Amer. Chem. Soc.*, 1923, **45**, 1460) that the analysis of the black oxide obtained by igniting praseodymium oxalate corresponds with that required by the formula Pr_6O_{11} within 1 per cent.

Neodymium chromate, $Nd_2(CrO_4)_3,8H_2O$.

$Nd_2O_3 = 43{\cdot}23$ (43·11); $CrO_3 = 38{\cdot}51$ (38·44).

Samarium chromate, $Sa_2(CrO_4)_3,8H_2O$.

$Sa_2O_3 = 45{\cdot}42$, 44·70 (44·00); $CrO_3 = 38{\cdot}10$, 38·23 (37·84).

Lanthanum chromate and praseodymium chromate are bright yellow, that of neodymium is dull yellow with a faint brown tinge, and samarium chromate is canary-yellow. These chromates form well-defined, microscopic, prismatic needles and appear to be isomorphous. The precipitates adhere tenaciously to the vessel. The data, with the exception of those for samarium chromate, are satisfactory. Samarium chromate is somewhat soluble in water, and the hydrion concentration attained on addition of sufficient potassium chromate to cause its separation is not much greater than that required for the precipitation of samarium hydroxide. (The precipitation of samarium hydroxide will be dealt with in a later paper.) The samarium chromates were, in consequence, slightly basic, although the greatest pains were taken to use the least possible amount of potassium chromate. Microscopic examination, however, showed that the precipitate was composed of monoclinic crystals similar to those of the other three chromates.

The following are the solubilities at 25° expressed in grams of anhydrous salt per 100 grams of water: $La_2(CrO_4)_3,8H_2O$, 0·020; $Pr_2(CrO_4)_3,8H_2O$, 0·021; $Nd_2(CrO_4)_3,8H_2O$, 0·027; $Sa_2(CrO_4)_3,8H_2O$, 0·043.

The chromates become less soluble at higher temperatures.

The power to form double chromates with potassium in presence of excess of potassium chromate is very marked in the case of lanthanum, praseodymium, and samarium. The addition of a large excess of potassium chromate effected, on boiling, the complete precipitation of each of the earths. When potassium chromate was added in excess to a chromic acid solution of lanthana, a potassium lanthanum chromate was precipitated. An excess of precipitant produced from a praseodymium solution a yellow precipitate, containing potassium and 39·80 per cent. of Pr_6O_{11} and 46·64 per cent. of

CrO_3, *i.e.*, 1 mol. of Pr_2O_3 : 3·97 mols. of CrO_3. As the precipitate was somewhat flocculent, it seems probable that it was a mixture of a double chromate and a little basic chromate.

The yellow samarium precipitate thrown down by the action of an excess of potassium chromate was much more flocculent and its composition and appearance varied with the amount of precipitant used. When a moderate excess was employed, the precipitate contained, besides much potassium, 33·02 per cent. of Sa_2O_3 and 41·40 per cent. of CrO_3, *i.e.*, 1 mol. of Sa_2O_3 : 4·37 mols. of CrO_3; with a large excess, 28·90 per cent. of Sa_2O_3 and 46·16 per cent. of CrO_3, *i.e.*, 1 mol. of Sa_2O_3 : 5·56 mols. of CrO_3. It was impossible to wash these precipitates completely and consequently some of the excess of CrO_3 was due to potassium chromate adsorbed by the basic samarium chromate which was certainly formed. The excess is, however, too great to be attributed entirely to adsorption and some must have been due to the formation of a double chromate of potassium and samarium. A phase-rule study is necessary to establish definitely the identities of these double chromates.

The precipitates obtained when potassium chromate was added to solutions of lanthanum salts were next examined. When more than 2 mols. of potassium chromate were added to 1 mol. of lanthanum nitrate, the yellow precipitates obtained were mixtures of the simple and a double chromate. Thus two typical precipitates contained 3·88 and 3·41 mols. of CrO_3, respectively, and 1 mol. of La_2O_3. The double chromate alone, however, was precipitated when the reactants were mixed in the reverse order. *M*/10-Lanthanum nitrate (100 c.c.) was added to an excess, 600 c.c., of *M*/10-potassium chromate, and the precipitate allowed to remain over-night in contact with the mother-liquor. It was microcrystalline, probably rhombic, and contained, in addition to potassium, lanthana and chromic anhydride in the proportion required by the formula $K_2CrO_4,La_2(CrO_4)_3,6H_2O$, *viz.*, $La_2O_3 = 35·21$ (35·14) and $CrO_3 = 43·39$ (43·13) per cent. The precipitate formed when a moderate excess of potassium chromate ($2\frac{1}{2}$ times the stoicheiometric amount) was added to a dilute solution of praseodymium chloride was the normal chromate, $Pr_2(CrO_4)_3,8H_2O$, in well-defined needles ($CrO_3 = 38·60$. Calc., 38·80 per cent.). The action of potassium chromate on a solution of a neodymium salt causes the precipitation of a mixture of the normal and basic chromates, whereas the precipitate obtained from a dilute samarium chloride solution is entirely basic, microscopical examination giving no indication of the normal chromate.

Discussion.

Of the chromates described in this paper, $La_2(CrO_4)_3,8H_2O$ is the only one mentioned in the literature (Abegg–Meyer, "Handbuch anorg. Chem.," 1906, Vol. 3 (1), p. 254).* The present author has been unable to confirm Frerichs and Smith's statement (*Annalen*, 1878, **191**, 363) that it is the anhydrous chromate which is precipitated under such conditions.

According to Krüss and Loose (*Z. anorg. Chem.*, 1893, **3**, 92), 'didymium" separates as a normal chromate, and erbium as a basic chromate in the same fraction, and does not form a double chromate with potassium. Although the pure double salt has not been isolated, there is evidence to show that praseodymium does form a double chromate; apparently neodymium does not do so.

Recalculation of the data recorded by Cleve (*Chem. News*, 1886, **53**, 100) for the precipitate he obtained by adding potassium chromate to excess of samarium nitrate indicates 1 Sa : 1·04 K : 1·93 CrO_4 : 1·58 H_2O, which is not in accord with the formula, $SaK(CrO_4)_2,3H_2O$, he proposed. The precipitate was probably a mixture of a double chromate and basic chromate, because basic precipitates only are obtained from dilute samarium chloride solutions. Böhm (*loc. cit.*) found that the order of precipitation in his chromate separations was lanthanum, praseodymium, neodymium, and lastly samarium. Some confirmation of this sequence is to be found in the gradual increase in the solubilities of the chromates at 25°; for lanthanum and praseodymium, the difference is so small as to be of little use in separation processes, but this is not the case with the other three elements, for which the chromate method was found to be valuable.

Contrary to the current view, all the rare-earth chromates, with the exception of those of cerium, so far encountered are yellow. Baur (D.R.-P. 120013, 1900) states that neodymium chromate is olive-brown; according to Orlov (*Chem.-Ztg.*, 1907, **31**, 562), it is moss-green; as obtained in the present work, it is dull yellow.

Many of the rare-earth chromates are basic. The only normal chromates which have been found hitherto belong to the "cerite" group, the bases of which are believed to be among the strongest of the rare earths. Even among the members of this group there is a gradually increasing tendency to form basic chromates in the case of the weaker bases, neodymia and samaria.

Summary.

(1) Lanthanum, praseodymium, neodymium, and samarium form isomorphous, yellow, sparingly soluble chromates of the general formula $M'''_2(CrO_4)_3,8H_2O$.

* The paper referred to is by Cleve, and contains no mention of the chromate.

(2) Owing to the difference in their solubilities, these are of importance in processes of fractional precipitation with potassium chromate.

(3) The tendency to form sparingly soluble double chromates is marked in the case of lanthanum, praseodymium, and samarium. Lanthanum forms the double salt $K_2CrO_4,La_2(CrO_4)_3,6H_2O$.

(4) The addition of potassium chromate to an aqueous salt solution causes the precipitation of (*a*) in the case of lanthanum, the simple chromate if the excess of precipitant is small, (*b*) praseodymium, the simple chromate, (*c*) neodymium, a mixture of simple and basic chromates, (*d*) samarium, a basic chromate of indefinite composition.

The author takes this opportunity to record his thanks to the Chemical Society for a grant from the Research Fund which defrayed the cost of the rare earths, and to the Department of Scientific and Industrial Research for a personal grant.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, April 30th,* 1924.]

CCXXXVII.—*Oxidation Potentials of Ferrous and Ferric Salts in Concentrated Hydrochloric Acid and Phosphoric Acid.*

By SYDNEY RAYMOND CARTER and FRANCIS HERBERT CLEWS.

SULPHUR dioxide is usually regarded as a reducing agent towards ferric salts, but this is only true in dilute acid solution, it having been shown that in strongly acid solutions sulphur dioxide reacts towards a ferrous salt as an oxidising agent (Wardlaw and Clews, J., 1920, **117**, 1093; Wardlaw, Carter, and Clews, *ibid.*, 1241). Obviously an investigation of the influence of acid concentration on the oxidation potentials of ferrous–ferric mixtures would assist in explaining this interesting phenomenon.

The oxidation potentials of ferrous and ferric chlorides in dilute (0·1*N*) hydrochloric acid solution have already been determined by Peters (*Z. physikal. Chem.*, 1898, **26**, 193), who also examined the effect of the addition of fluorides and chlorides on the oxidation potentials.

The present paper is concerned with a study of the oxidation potential in concentrated hydrochloric and phosphoric acid respectively.

Ferrous–Ferric Cell.—Ferrous chloride solutions were prepared from iron and hydrochloric acid under exclusion of air, whilst those

of ferric chloride were obtained by dissolving solid anhydrous ferric chloride in hydrochloric acid. The total iron content was arranged in all cases to be about 0·2 gram-molecule per litre, the concentration of the hydrochloric acid being varied in the different experiments. The relative amounts of ferrous and ferric chlorides were determined after the *E.M.F.* measurements by titration with $N/10$-potassium dichromate by Zimmermann and Reinhardt's method. The total chlorides were determined by titration with silver nitrate and ammonium thiocyanate solutions. From these estimations the free hydrochloric acid could be calculated.

The oxidation cell was furnished with several electrodes, some being of platinum foil whilst others were glass tubes coated with platinum; in all cases they gave concordant results. An atmosphere of carbon dioxide was maintained above the solution.

A syphon tube filled with the same solution as the cell was connected with the normal calomel electrode ($E = 0{\cdot}560$ volt) through a N-solution of potassium chloride for the electrometric measurements. The calomel electrode has certain disadvantages when working with strongly acid solutions, but its behaviour was investigated with the object of comparing the results obtained with those of Peters.

The measurements were controlled in most cases by means of mercurous sulphate electrodes and hydrogen electrodes as an additional precaution.

All concentrations are given in gram-molecules per litre and are denoted by square brackets. The concentrations of the ferrous and ferric radicals are denoted by $[Fe^{II}]$ and $[Fe^{III}]$, respectively, if they refer to salt concentrations. Ionic concentrations are denoted thus, $[Fe^{\cdot\cdot}]$ and $[Fe^{\cdot\cdot\cdot}]$.

Variation of Oxidation Potential with the Proportion of Ferric Iron.—In order to test the validity of the logarithmic formula for change in the relative proportions of ferrous and ferric iron, several cells were made up with the same concentration of hydrochloric acid but with varying proportions of ferric iron, and the potential, E_c, was measured against a normal calomel electrode. E_{oc} is the potential when the concentrations of ferric and ferrous iron are equal and is calculated from the formula

$$E_{oc} = E_c - 0{\cdot}058 \log [Fe^{III}]/[Fe^{II}].$$

The results are given in Table I and the constancy of E_{oc} is a good verification of the applicability of the formula. A small correction might be introduced to reduce the *E.M.F.* to the same acid concentration; the effect, however, is small and practically within the experimental error.

TABLE I.*

Variation of Potential with the Proportion of Ferric Iron.

[HCl].	$[Fe^{III}]/[Fe^{II}]$.	$\frac{[Fe^{III}]}{[Fe^{III}]+[Fe^{II}]} \times 100.$	*E.M.F.* obs. E_c (volt).	Normal *E.M.F.* $[Fe^{III}] = [Fe^{II}]$. E_{oc} (volt).
9·58	0·0229/0·1436	13·8	0·1318	0·1780
9·62	0·0702/0·0822	46·1	0·1747	0·1787
9·60	0·1113/0·0302	78·6	0·2097	0·1775

* The measurements were confirmed by Mr. F. M. Lea, M.Sc., to whom our thanks are due.

The logarithmic relation is thus available for transforming from one value of $[Fe^{III}]/[Fe^{II}]$ to another.

The Influence of Concentration of Hydrochloric Acid on Oxidation Potential.—The potentials, E_c, of a series of electrodes in solutions containing approximately constant proportions of ferrous and ferric iron and varying concentrations of hydrochloric acid were determined. The values were finally reduced by means of the formula $E_{oc} = E_c + 0{\cdot}058 \log [Fe^{II}]/[Fe^{III}]$ to the normal oxidation potential, E_{oc}, which corresponds with equal amounts of ferrous and ferric iron.

E_0 represents the oxidation potential after allowing 0·560 volt for the normal calomel electrode. The results are given in Table II.

TABLE II.

Cell No.	Concentration in gram-mol. $[FeCl_2]$.	$[FeCl_3]$.	[HCl].	$\frac{[Fe^{II}]}{[Fe^{II}]+[Fe^{III}]} \times 100.$	*E.M.F.* in volt. E_c.	E_{oc}.	E_0.
2	0·0501	0·0306	0·1	62·1	+0·416	+0·428	+0·988
6	0·0536	0·0328	0·910	62·0	0·376	0·388	0·948
7	0·0592	0·0341	2·119	63·5	0·348	0·362	0·922
8	0·0524	0·0326	4·032	61·7	0·303	0·315	0·875
9	0·0441	0·0440	4·820	50·0	0·298	0·298	0·858
10	0·0565	0·0357	5·606	61·3	0·275	0·287	0·847
1	0·0463	0·0298	10·02	60·9	0·168	0·179	0·739

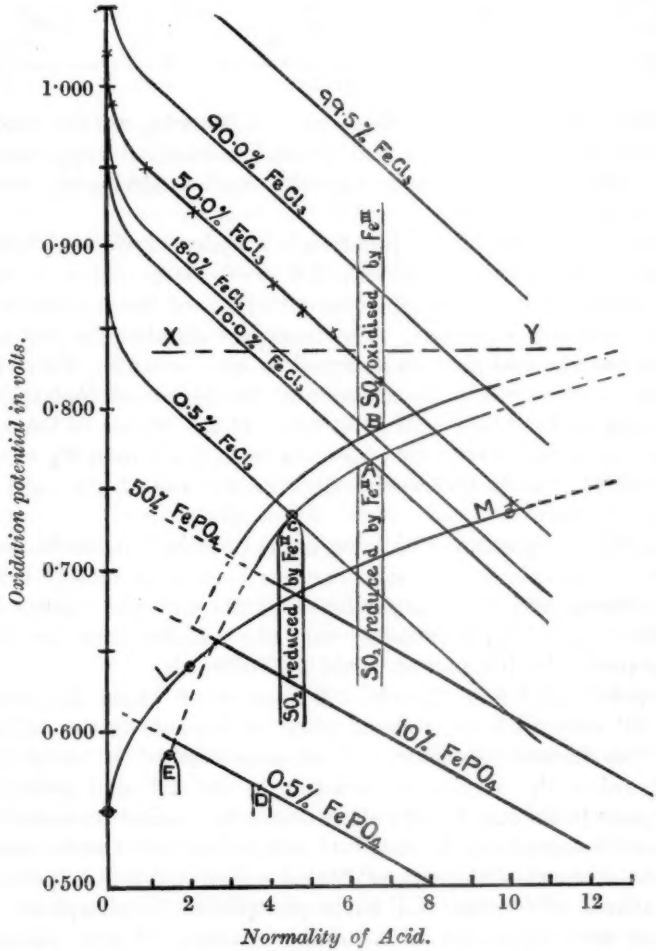
For comparison some of the values given by Peters (*loc. cit.*) for low concentrations of acid (below 1·0*N*) may be quoted. The total iron concentration varies between wide limits, but this does not appear to have any great influence. In all cases $[FeCl_3]$ was equal to $[FeCl_2]$.

TABLE III.

Total iron. Gm.-mol.	[HCl].	*E.M.F.* in volt. E_{oc}.	E_0.
0·313	0·0313	+0·439	+0·999
0·1	0·1	0·427	0·987
0·5	0·5	0·400	0·960
0·0625	0·938	0·389	0·949

It will be noticed that the oxidation potential falls off with increasing concentration of acid, and on plotting the values of Table II (Fig. 1) the potential is seen to decrease linearly with the normality

FIG. 1.

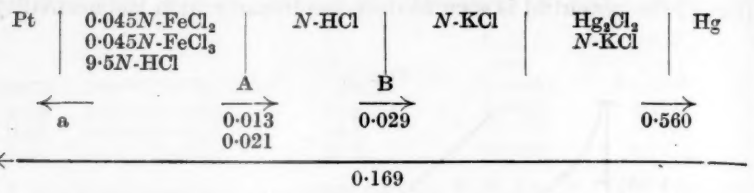


Oxidation potentials of ferrous–ferric salts in hydrochloric acid and phosphoric acid.

of the hydrochloric acid for concentrations between 1·0*N* and 10*N*. The total change involved is considerable.

The Diffusion Potential.—In view of the high concentration of acid, the diffusion potential requires special consideration.

The following cell was made up and its total *E.M.F.* found to be 0·169 volt.



A potential is set up at the junction B owing to the unequal velocities of the hydrogen- and potassium-ions; its approximate value, calculated from the formula $E_B = 0{\cdot}058 \log (u_{H} + v_{Cl'})/(u_{K\cdot} + v_{Cl'})$, is 0·029 volt.

The boundary A, like the junction in a hydrochloric acid concentration cell, gives rise to a potential $E_A = 0{\cdot}058(u - v)/(u + v) . \log C_1/C_2$, where C_1 and C_2 are the concentrations of the hydrogen-ions in the respective solutions. The transport number for the anion of hydrochloric acid may be assumed to be $n = 0{\cdot}17$. There is an element of uncertainty in estimating the degree of ionisation in the strong hydrochloric acid solutions. If the degree of ionisation is based on conductivity data alone ($\alpha = \Lambda_v/\Lambda_\infty$), then $E_A = 0{\cdot}013$ volt, whilst conductivity–viscosity data ($\alpha = \Lambda_v\eta_v/\Lambda_\infty\,\eta_0$) give $E_A = 0{\cdot}021$ volt.

Since the completion of this work the potential at the boundary between hydrochloric acid solutions has been more closely investigated (Carter and Lea, unpublished work) and the results show that the value of E_A is probably very much higher than the above. In this particular instance it would be 0·079 volt.

The potential at B (0·029 volt) will be constant, whilst the potential at A will vary with the concentration of the acid in the oxidation cell. The highest concentration of acid studied is about 9·5*N*, and therefore the maximum variation in the diffusion potential is inadequate to account for the alteration in the oxidation potential of ferric and ferrous chlorides in dilute and concentrated acid solutions.

Ferric–Ferrous Phosphate Potential.—The oxidation potentials of mixtures of ferrous and ferric phosphates in phosphoric acid solution were measured in a similar manner. Ferric phosphate was dissolved in phosphoric acid of known strength and ferrous phosphate prepared by dissolving iron wire in phosphoric acid of similar concentration. The free phosphoric acid was calculated by difference. The relative amounts of ferrous and ferric iron were determined subsequently by titration with potassium dichromate in presence of an excess of hydrochloric acid. The total iron concentration was approximately 0·1 gram-molecule per litre.

TABLE IV.

Oxidation Potential of Ferrous–Ferric Phosphates in Phosphoric Acid.

		E.M.F. in volt.				Corrected for diffusion potential.
$[H_3PO_4]$.	$\frac{[Fe^{III}]}{[Fe^{II}]+[Fe^{III}]}$.	E_c.	E_{oc}.	E_0.	π.	E_0 (corr.).
4·318	50·6	+0·126	+0·122	+0·684	−0·027	+0·711
7·279	51·8	+0·089	+0·087	+0·647	−0·028	+0·675
15·79	53·4	−0·034	−0·037	+0·523	−0·020	+0·543

The oxidation potential of the ferrous–ferric mixture diminishes considerably on addition of phosphoric acid and the question arises whether the change is due to the diffusion potential at the acid–salt boundary. An estimate of the diffusion potential at the junction x*N*-H_3PO_4/*N*-KCl has been made on the basis of Henderson's formula (*Z. physikal. Chem.*, 1908, **63**, 325), and the values are given under column π, whilst column E_0 (corr.) gives the potential after applying this correction.

It will be seen that the diffusion potential does not account for the depression in oxidation potential.

It is found graphically that the decrease in potential varies almost linearly with increasing concentration of phosphoric acid. It will also be noticed that the oxidation potential of the ferric–ferrous phosphate mixtures falls much lower than those of the ferric–ferrous chloride mixtures for the same acid normality and the same $[Fe^{III}]/[Fe^{II}]$ ratio.

Discussion of the Causes of the Change in Oxidation Potential due to Acid Concentration.—(A) *Hydrochloric Acid.* The behaviour of oxidation cells may usually be explained by a consideration of the formula $E = E_0 + 0{\cdot}058 \log [Fe^{\cdot\cdot\cdot}]/[Fe^{\cdot\cdot}]$, where E_0 corresponds with the potential of a mixture of $Fe^{\cdot\cdot\cdot}$- and $Fe^{\cdot\cdot}$-ions in equal proportions and E is the observed potential for any given ratio of $[Fe^{\cdot\cdot\cdot}]/[Fe^{\cdot\cdot}]$.

Owing to complex formation, it is difficult to obtain an accurate measure of the ratio $[Fe^{\cdot\cdot\cdot}]/[Fe^{\cdot\cdot}]$. There is, however, less tendency towards complex formation in the case of the nitrates and, since these salts are appreciably dissociated, Maitland (*Z. Elektrochem.*, 1906, **12**, 263) was able to deduce the normal potential, when equivalent amounts of ferrous and ferric ions were present, as $E_{ho} = 0{\cdot}743$ volt at 25°. On the absolute scale this corresponds with $E_{ao} = 1{\cdot}020$ volts. Peters's investigations on the chlorides show a lower potential than this, even in the most dilute acid (0·0313 *N*-HCl, $E_0 = 0{\cdot}999$ volt at 17°).

The effect of continued addition of acid, shown by the experiments of Peters with 0·0313*N*- to *N*-hydrochloric acid and by those of

the present authors with 0·1*N*- to 10*N*-hydrochloric acid, is to produce a steady fall in the oxidation potential (see Fig. 1, curve $FeCl_3$ 50 per cent.).

It follows, therefore, that there is a gradual change in the ratio $[Fe^{\cdot\cdot\cdot}]/[Fe^{\cdot\cdot}]$ and this is probably due to the disappearance of ferric ions owing to the formation of a complex between ferric chloride and hydrogen chloride.

$$FeCl_3 = Fe^{\cdot\cdot\cdot} + 3Cl' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$FeCl_3 + nHCl = FeCl_3,nHCl \quad . \quad . \quad . \quad . \quad (2)$$

In this connexion it may be mentioned that several compounds of the following types are known: $FeCl_3,MCl$, $FeCl_3,2MCl$, and $FeCl_3,3MCl$, where M is a univalent metal. In the case of hydrogen chloride, however, only compounds of the type $FeCl_3,HCl$ have been isolated. Ferrous chloride gives rise to compounds of the types $FeCl_2,MCl$ and $FeCl_2,2MCl$, but up to the present no acid chlorides have been described.

It is thus reasonable to suppose that the double chloride $FeCl_3,HCl$ is formed in solution with increasing acid concentration, whilst the ferrous chloride forms no complex with hydrochloric acid at all.

(B) *Phosphoric Acid.* From the fact that both the ferrous and ferric phosphates are insoluble in pure water but soluble in phosphoric acid, it is probable that practically all the iron is held in the form of complexes, and consequently the amounts of ferric and ferrous iron in the ionic state are extremely small.

The addition of phosphoric acid brings about a considerable diminution in the oxidation potential, and from this we should infer that complex formation is much greater in the case of ferric than ferrous phosphate.

Action of Sulphur Dioxide on Ferrous and Ferric Salts.—The variation in the oxidation potential of ferrous and ferric salts with concentration of hydrochloric acid and phosphoric acid respectively is shown graphically in Fig. 1. The line "50 per cent. $FeCl_3$" gives the oxidation potential of a mixture containing equal proportions of ferric and ferrous radicals. The successive parallel lines correspond with mixtures containing varying amounts of ferric iron, indicated by the percentages.

The drop in oxidation potential of ferric–ferrous chloride is considerable, and to a substance which is unaffected by the acid concentration, and the oxidation potential of which is represented by the line *XY* (say), a 50 per cent. mixture of ferric–ferrous chloride is an oxidising agent at low acid concentrations (*e.g.* *N*-HCl) and a reducing agent at high acid concentrations (10*N*-HCl).

It now becomes of interest to consider the remarkable behaviour

of sulphur dioxide as a reducing agent towards ferric salts in dilute acid solution and as an oxidising agent in strongly acid solution (J., 1920, **117**, 1093, 1243).

It was found (*ibid.*, 1100) that ferrous chloride was oxidised by sulphur dioxide provided the quantity of ferric iron was not greater than 10·0 per cent., whilst ferric chloride was reduced by sulphur dioxide provided the ferric iron was not less than 18·0 per cent. The concentration of hydrochloric acid was 6·5*N*. Hence the lower limit of 10 per cent. of ferric iron and 90 per cent. of ferrous iron is given by *A*, at which the oxidation potential is 0·765 volt. Similarly, the upper limit, 18 per cent. of ferric iron and 82 per cent. of ferrous iron, is given by *B* and corresponds with a potential of 0·783 volt.

A further point, *C*, is given by the observation (*ibid.*, 1098) that a solution of ferrous chloride (which may be assumed to have an approximate composition of 99·5 per cent. $FeCl_2$ and 0·5 per cent. $FeCl_3$ *) is just able to reduce sulphur dioxide in a solution of 4·5 *N*-hydrochloric acid (165 grams HCl per litre).

Also a point *E* is given by the fact that sulphur dioxide just fails to be reduced by a solution of cuprous chloride in 1·5*N*-hydrochloric acid (J., 1922, **121**, 215), since a cuprous chloride solution (cuprous/cupric = 99·5/0·5) in 1·5*N*-hydrochloric acid gives $E_a = 0{\cdot}583$ (uncorrected for diffusion potential) (Carter and Lea).

Points *A*, *C*, and *E* thus mark limiting values for sulphur dioxide as an oxidising agent, and *B* its limit as a reducing agent. If the reactions for sulphur dioxide were well-defined and reversible, the points *A* and *B* should coincide and lie on a curve representing the oxidation–reduction potential curve of sulphur dioxide. It is probable, however, that the reactions are not sufficiently reversible for a well-defined line to be traced and it would only be possible to give a band over which sulphur dioxide behaves as neither a reducing nor an oxidising agent.

It should be noted that the effect of temperature has not yet been considered. The potential measurements were made at 17° and the oxidation experiments with sulphur dioxide and ferrous–ferric salts at about 100°. The deductions from these results, however, are of a qualitative nature only, and the general relations of the ferric–ferrous potential and the sulphur dioxide potential will be as indicated.

Referring to the lower portion of the graph, the very low value of

* In the oxidation experiments quoted, ferrous chloride was acted upon by sulphur dioxide for several hours. Control experiments in absence of sulphur dioxide showed that ferrous chloride could not be obtained free from ferric salt; by careful working, the quantity of the latter could be diminished to 0·7—0·5 per cent.

the oxidation potential of ferric–ferrous phosphate at once explains several interesting facts. Ferrous phosphate in phosphoric acid solution is more readily oxidised by sulphur dioxide than is ferrous chloride in hydrochloric acid (J., 1920, **117**, 1241). Ferric phosphate in phosphoric acid solution requires a very powerful reducing agent to convert it into the ferrous condition (J., 1923, **123**, 2381), and it is not reduced at all by sulphur dioxide (J., 1920, **117**, 1242).

It may be noted that, over a wide range of concentrations, conductivity and other results indicate that only the first hydrogen atom ionises in phosphoric acid, which has therefore been regarded as a monobasic acid and the normality with respect to molar weight plotted.

The point D ($E_a = 0{\cdot}560$ volt. uncorr.) represents a $3{\cdot}8N$-solution of phosphoric acid and at this concentration ferrous phosphate just reduces sulphur dioxide (J., 1920, **117**, 1244, 1245). The line *ACE*, however, which refers to the strong acid, hydrogen chloride, can scarcely be expected to pass through the point D obtained with phosphoric acid, which is relatively much weaker.

Summary.

1. The oxidation potentials of the ferric and ferrous salts have been determined in concentrated hydrochloric acid and phosphoric acid respectively.

2. The logarithmic law has been shown to hold for variations of the ratio of the ferric–ferrous radicals in concentrated acid solution.

3. Increasing concentration of acid causes a decrease in the oxidation potential in each case, and this is attributed to the formation of complexes.

4. The diffusion potential is insufficient to account for this change in potential.

5. The potentials have been plotted against acid concentrations and discussed in the light of the action of sulphur dioxide on ferrous and ferric salts.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

[*Received, April 26th*, 1924.]

CCXXXVIII.—*The Composition and Properties of Clay.*

By ALFRED FRANCIS JOSEPH and JOHN STANLEY HANCOCK.

THE object of the present communication is to record the composition of a number of clays (principally soil clays) together with some physical and chemical properties which appear correlated with composition. The term "clay" is used throughout to denote that

portion of the raw material which will remain suspended in a column of water 10 cm. high for 8 hours : assuming Stokes's law to hold good, this corresponds to a maximum diameter of 0·002 mm.

In this way comparatively homogeneous preparations are obtained and relationships can be observed which would be obscured altogether if coarser materials were examined.

An illustration will show the important difference in composition of fine and coarse "clay" fractions. Mechanical analysis of a red soil from Kordofan showed that 67·1 per cent. consisted of particles smaller than 0·2 mm., but only 29·5 per cent. smaller than 0·002 mm. : the larger fraction was found to contain 70·15 per cent. of silica, but the smaller one only 42·08 per cent. Now it is obviously useless to attempt to connect the clay-like properties of the 0·2 mm. fraction with its composition, because it contains a large amount of coarse material from which these properties are absent. The point may perhaps be further illustrated by comparing these figures with the composition of a very highly plastic clay (bentonite), containing 68·68 per cent. of silica. This would suggest an analogy in composition with the Kordofan coarse material which is altogether false, the fact being that the bentonite is comparatively homogeneous, whilst the Kordofan product contains about 30 per cent. of fine quartz in addition to the clay proper.

Raw Materials Examined.—In the course of this work, clays have been separated and examined from the sources shown in the table below :

TABLE I.

Reference No.	Description.	Locality.	Colour.	Mechanical composition. % less than 0·2 mm.	% less than 0·002 mm.
10118	China clay.	England.	White.	100	12·8
10120	Ball clay.	,,	,,	99·7	89·8
10468	Soil clay.	N. Wales.	Brown.	97·9	62·0
F.E.	Fullers earth.	Purchased.	Light brown.	100	87·9
9650	Potting clay.	Luxor, Egypt.	Yellow.	100	46·8
10743	Bentonite.	B. Columbia.	White.	100	85·1
10744	,,	Alberta.	,,	100	83·5
6640	Soil clay.	Blue Nile, Sudan.	Brown.	87·2	57·2
6960	,,	Kordofan, Sudan.	Black.	98·4	68·1
9228	,,	White Nile, Sudan.	Slate.	98·1	71·4
8320	,,	Kassala, Sudan.	Brown.	94·6	46·7
7897	,,	Kordofan, Sudan.	Red-brown.	69·6	17·3
7900	,,	Kordofan, Sudan.	Red.	67·1	29·5
9223	,,	Tokar, Sudan.	Brown.	99·9	29·8

Methods of Preparation and Analysis.—The mechanical analysis of the raw material has been made according to the method used for soils in these laboratories (Joseph and Martin, *J. Agric. Sci.*, 1921, **11**, 239), and the chemical analysis by that of the United States Geological Survey (Hillebrand, *U.S. Geol. Survey Bull.*, No. 700, 1919). The separation of the purified clay fractions is made by deflocculating the material with sodium carbonate and allowing to settle for 8 hours to a depth of 10 cm. exactly as is done in mechanical analysis. The clay suspensions are then flocculated with a trace of acid and purified from electrolyte until the high specific resistance of the suspension shows the process to have been carried sufficiently far. The resistance can easily be raised to 50,000 or even 100,000 ohms either by dialysis or by filtration, using collodion filters. Details as to the former have already been published (Joseph and Martin, *J. Agric. Sci.*, 1923, **12**, 49, appendix). In the other method, a collodion filter is prepared by pouring a few cubic centimetres of collodion on to a filter-paper cemented round the edge to a Buchner funnel by means of ordinary cycle rubber solution, allowing the film to dry, and washing by sucking water through it.* Such a filter will retain clay completely, the filtrate being quite bright and clear, and by filtering a clay suspension, removing the clay from the filter, shaking with water, and again filtering (this operation being repeated as many times as are necessary) the electrolyte concentration may be reduced to a very small amount.

Chemical Composition of the Clays Examined.—The detailed results of the chemical analyses are given in the table below, the last column giving the molecular ratio of silica to alumina. With the data at present available we consider that this ratio is by far the most important chemical constant of a clay, and therefore the clays are arranged in order according to its magnitude.

They divide themselves in this way into three groups, namely, those in which the ratio is less than 3, between 3 and 5, and above 6, respectively, and it can certainly be said that, judging them empirically (literally by rule of thumb), they fall into the same classes with respect to their plastic properties. Thus the list begins with what is nearly pure kaolinite (non-plastic), and ends with the fine fraction obtained from bentonite, an extremely plastic material possessing "clay" properties to an exaggerated degree ("The Mineral Bentonite: its occurrence and uses," *Bull. Imp. Inst.*, 1922, **20**, 344) and, as shown by Hall ("Tech. Paper U.S. Bureau

* We are indebted to Mr. J. A. Prescott of Cairo and Dr. F. J. Martin of these laboratories for the details for making these very convenient and simple filters.

TABLE II.

Chemical Analyses of Fraction Consisting of Particles less than 0·002 mm. in Diameter.

Ref. no.	SiO_2.	Al_2O_3.	Fe_2O_3.	TiO_2.	MnO.	CaO.	MgO.	Vol. matter.	Na_2O.	K_2O.	Total.	Ratio SiO_2/Al_2O_3.
10118	46·77	37·60	1·14	0·23	0	0·94	0·21	12·44	0	0·88	100·21	2·11
10120	49·26	31·39	3·86	1·77	0	0·87	0	10·90	0·18	0·94	99·17	2·66
10468	44·90	26·81	8·63	1·63	0·20	0·88	2·12	10·48	1·42	1·75	98·82	2·84
7900	42·08	25·10	14·38	2·78	0	0·80	0·64	13·14	0·51	1·28	100·71	2·85
8320	44·58	19·98	14·41	1·42	0·24	1·18	2·95	14·17	0·18	1·35	100·46	3·77
6640	46·70	20·22	12·44	2·03	0	1·10	1·59	15·16	0·48	0·54	100·26	3·90
9223	46·19	19·99	14·30	1·45	trace	1·05	3·61	12·73	0·72	0·39	100·43	3·93
6960	48·35	20·72	13·14	2·90	0	1·26	0·56	12·66	0·79	0·35	100·73	3·95
9650	45·45	17·99	10·26	1·80	0·23	6·23	3·91	11·15	1·60	0·61	99·23	4·28
7897	48·32	18·57	16·69	2·27	0·37	0·93	1·57	11·55	0·93	0·34	101·54	4·41
F.E.	54·26	19·24	7·66	1·35	0	0·93	3·44	10·29	2·42	trace	99·59	4·77
9228	48·77	17·27	15·48	3·12	0	1·35	0·80	12·97	0·17	0·38	100·31	4·79
10743	68·29	16·62	4·25	0·49	0·59	1·15	1·17	6·63	1·31	0·35	100·85	6·96
10744	68·34	15·10	3·65	0·34	0	0·83	1·80	8·32	2·14	0	100·52	7·67

Standards," No. 234, 1923), capable of increasing the plasticity of a "lean" material such as china clay.

Relation between Composition and Properties.—We have naturally been anxious to follow up this slender indication that "plasticity" is related to the silica–alumina ratio. Plasticity, however, the really characteristic property of clay, has so far baffled all attempts to measure it. Mechanical tests have been devised and various indirect methods have been used based on the measurement of other properties (such as shrinkage or the adsorbing power for dyes) usually found associated with plasticity. None has proved satisfactory and we now somewhat diffidently put forward the suggestion that the chief characteristic of the "plasticity" of a clay is that it is a property which above all others is affected by the action of heat and electrolytes, so that if some property be chosen which is possessed by all "clays," whether of high or low plasticity, the effect of heat or of electrolytes in modifying it might afford a measure of plasticity.

The property which has proved of most interest to us for this purpose is the "moisture equivalent," that is, the percentage of water which is retained by the material after being saturated for 24 hours and then drained in a Briggs-Maclane centrifuge for 40 minutes by a force equal to 1000 times that of gravity. The results obtained in these laboratories by this method have been described (*J. Agric. Sci.*, 1923, **12**, 49).

Some of the results are given below, the figures giving the moisture equivalent of some soils and clays under ordinary conditions, after ignition, and without ignition, but when saturated with 3 per cent. of sodium carbonate solution instead of with pure water.

TABLE III.

Substance.	% Clay.	Silica–alumina ratio in clay.	Moisture equivalent. Usual method.	After ignition.	With sodium carbonate.
Kaolin	59·0	2·0	44·0	58·0	49·0
10118 clay from China clay	100·0	2·1	44·4	57·8	38·6
10120K clay from ball clay	100·0	2·7	55·0	41·6	54·7
7900K Red soil clay	100	2·9	38·1	27·7	54·3
6640 Loess soil	57·5	3·9	37·8	11·1	51·3
6640K clay from Loess soil	100	3·9	53·2	9·8	89·5
9320 Blue clay soil	51·6	4·8	48·5	13·8	—
10743 Bentonite	85·1	6·9	118	47·1	180

The differences in behaviour are very striking, kaolin and non-plastic China clay losing none of their water-retaining capacity by ignition and gaining nothing in this respect by treatment with alkali. The ball clay and red soil clay undergo changes, but these are small compared with those of the three plastic substances which

occur next in the list, whilst the very plastic bentonite has its moisture equivalent reduced 70 per cent. by ignition and increased 60 per cent. by treatment with sodium carbonate.

Composition and Chemical Properties of Clay.—A clear idea as to the chemical nature of clay will probably not be obtained without a study of the silicates and alumino-silicates high in silica, concerning which little is known. Small quantities of substances other than silica and alumina may, of course, exert a great influence on properties, but a comparison of the composition of the non-plastic China clay and bentonite clay does not indicate this :

TABLE IV.

	SiO_2/Al_2O_3.	$SiO_2+Al_2O_3$.	$CaO+MgO$.	Na_2O+K_2O.	Fe_2O_3.
China clay 10118	2·11	84·37	1·15	0·88	1·14
Bentonite 10743	6·96	84·91	2·32	1·66	4·25

The figures suggest that only in the great difference between the ratios of the first-mentioned constituents is a chemical constant related to physical properties likely to be found.

In their chemical properties, clays are in many cases reactive in proportion to the amount of silica they contain, and a good example of this is their behaviour towards alkali. Preliminary experiments have been carried out by observing the change which takes place when suspensions of different clays are added to sodium hydroxide (about $N/100$) and the mixtures kept for 24 hours. The change can conveniently be followed by observing the conductance of the mixture, any disappearance of hydroxyl-ion being accompanied by a fall in conductance owing to the high mobility of this ion (174 at 18°).

The following figures give the specific conductance, multiplied by 10^4, of the sodium hydroxide solution used (corrected for the volume of clay suspension added) before and after the addition of clay in the proportion of 0·1 gram to 100 c.c. of alkali.

TABLE V.

		Specific conductance of alkali.		
Material.	SiO_2–Al_2O_3 ratio.	Alone.	24 Hours after addition of clay.	Percentage reduction.
China clay 10118	2·11	37·28	36·07	3
Loess clay 10195	3·90	37·80	35·61	6
Bentonite clay 10743	6·96	38·31	34·72	9
Pure silica powder ...	∞	38·06	28·94	24

The method is, of course, a rough one, but the reactivity of the silica is clearly brought out in these cases : pure kaolinite with

a silica–alumina ratio of 2·0 would probably be non-reactive towards dilute alkali.

One of the most important properties of clays is that they possess the power of exchanging bases with electrolytes, this well-known phenomenon having been first described by Way. If clays are salts of an alumino-silicic acid which still contains replaceable hydrogen, "base exchange" on the addition of a neutral sodium salt might include the replacement of hydrogen for sodium as part of the process and thus lead to the development of acidity in the solution. In the simple case of silica itself, this happens quite readily and details relating to reactions, between silica and electrolytes, which are accompanied by the liberation of hydrogen-ions have recently been published by us (J., 1923, **123**, 2022). Similar effects are shown by clays, and the figures given below for the materials in Table V suggest that the silica–alumina ratio is correlated with the extent to which acidity is developed.

The acidity is indicated by the hydrogen-ion concentration of the clay suspension to which sodium chloride has been added, the suspension being then kept for 24 hours. All measurements were made electrometrically with a Leeds and Northrup potentiometer.

TABLE VI.

Material.	Silica–alumina ratio.	p_H Value after addition of salt solution.
China clay 10118	2·11	7·16
Loess clay 10195	3·90	5·15
Bentonite clay 10743 ...	6·96	4·12
Pure silica	∞	3·96

It is generally believed that the property of base exchange possessed by clays is lost on ignition. We have not made any experiments to test the exchange of one metal for another: we have found, however, that ignition may reduce, but does not destroy, the power of a clay to develop acidity on the addition of a neutral electrolyte.

Summary.

(1) Investigations on the relationship between the composition and properties of clays must be made with the aid of homogeneous preparations, the coarser portions being rejected as far as possible.

(2) The ultimate analysis of a number of clay separates showed wide differences in chemical composition, the most important characteristic appearing to be the silica–alumina ratio.

(3) This ratio seems connected with essential "clay" properties, being low in non-plastic and high in plastic materials.

(4) It is suggested that a property (such as the moisture equivalent)

which is greatly modified by ignition and electrolytes might afford a measure of plasticity for practical purposes: the silica–alumina ratio appears connected with the extent of these modifications.

(5) The same constant seems related to the chemical reactivity shown by different clays towards sodium hydroxide and neutral electrolytes; in the latter case, the development of acidity is regarded as a special case of base exchange.

Our thanks are due to Mr. J. W. Farmery for making some of the chemical analyses and to Dr. F. J. Martin for making the p_H measurements and some of the clay preparations.

WELLCOME TROPICAL RESEARCH LABORATORIES,
KHARTOUM. [*Received, April 12th*, 1924.]

CCXXXIX.—*Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part V. Rotatory Dispersions of* d-*Camphorimide,* d-*Camphorbenzylimide, Benzyl*-d-*camphoramic Acid, and their Derivatives.*

By BAWA KARTAR SINGH and ATUL CHANDRA BISWAS.

THE rotatory powers of a number of benzyl and substituted benzyl derivatives of *d*-camphorimide and of *d*-camphoramic acid for three wave-lengths and six solvents have been studied with the object of finding some relation between their optical activity and chemical constitution, and the following conclusions drawn.

(1) The effect of substituting the benzyl group for the imido-hydrogen atom is to increase the rotatory power.

(2) The influence of the solvent on the rotatory power is considerable. The order of the dielectric constants of the solvents employed is benzene (2·3)<ether (4·3)<chloroform (5·2)<acetone (21·2)<ethyl alcohol (26·0)<methyl alcohol (32·5). In all cases except one (camphor-*o*-nitrobenzylimide) the rotatory power is lowest in benzene, which has the lowest dielectric constant. The rotatory powers in the other solvents, however, vary irregularly; and in particular they do not run parallel to the dielectric constants of the solvents, nor disclose any relation between them. A more rational method, however, would be to correlate the rotatory power with the dielectric constant of the corresponding *solution* and not of the pure solvent.

The rotatory dispersion of *d*-camphorimide and its benzyl derivatives is highest where the rotatory power is lowest. Conversely,

the rotatory dispersion of camphor-*o*-nitrobenzylimide is lowest in benzene, where its rotatory power is highest. It would therefore seem that, in this series, the rotatory power and the rotatory dispersion are influenced in opposite directions by the change from one of the five aliphatic solvents to benzene.

(3) The relative magnitude of the rotatory power of camphorbenzylimide and its three nitro-derivatives varies with the nature of the solvent. Thus the order of magnitude is reversed in chloroform and in benzene. Frankland's rule is followed only in the case of these two solvents. Cohen's rule, on the other hand, is followed in the case of four solvents, but not in the case of the other two, namely, chloroform and methyl alcohol. The difference in the molecular rotatory power in chloroform between the ortho- and the unsubstituted compound is 8·8°; and that between the para-derivative and the unsubstituted compound is 10·3°. This deviation from Cohen's rule is insignificant, but that in methyl alcohol is very marked.

(4) Opening the ring structure of the above compounds by hydrolysis increases the rotation very considerably. (The rotatory power of *o*- and *p*-nitrobenzylcamphoramic acids could not be determined owing to their being insoluble in the ordinary solvents.) Thus the following are the values of $[M]_D$ in ethyl alcohol: camphorimide 10·99°, camphoramic acid 89·45° (α), 119·4° (β); camphorbenzylimide 30·19°, benzylcamphoramic acid 99·88°; camphor-*m*-nitrobenzylimide 31·92°, 3-nitrobenzylcamphoramic acid 106·70°.

(5) The *o*-, *m*-, and *p*-nitrobenzylcamphoramic acids exist in two modifications, distinguished by their melting point or colour. The tertiary aryl derivatives of *d*-camphorimide yield, on hydrolysis, monobasic acids containing both a carboxyl group and a substituted acid amide group; and since these two groups are differently disposed in the molecule, two compounds are formed.

$$C_8H_{14}\begin{matrix}CO\cdot OH\\CO\cdot NHR\end{matrix} \xleftarrow{H_2O} C_8H_{14}\begin{matrix}CO\\CO\end{matrix}NR \xrightarrow{H_2O} C_8H_{14}\begin{matrix}CO\cdot NHR\\CO\cdot OH\end{matrix}$$

This isomerism is therefore structural, and is of the same nature as that of the α and β- camphoramic acids.

EXPERIMENTAL.

d-Camphorimide was prepared by Bredt's method (*Annalen*, 1903, **328**, 344), and *d*-camphorbenzylimide and *d*-camphor-*p*-nitrobenzylimide by Evans's method (J., 1910, **97**, 2237).

d-*Camphor*-o-*nitrobenzylimide*, $C_8H_{14}\begin{matrix}CO\\CO\end{matrix}N\cdot C_7H_6\cdot NO_2$.—A solution of 10 gms. of camphorimide and 9·5 gms. of *o*-nitrobenzyl chloride in 45 c.c. of 1·125*N*-alcoholic potassium hydroxide was

heated for 45 minutes on the water-bath, cooled, and the alcohol evaporated off. The residue, after being washed with dilute aqueous sodium hydroxide, crystallised from hot alcohol in long, pale yellow, rectangular needles, m. p. 131°. 0·1380 gave 10·6 c.c. N_2 (moist) at 740 mm. and 15·2°. N = 8·94 ($C_{17}H_{20}O_4N_2$ requires N = 8·86 per cent.).

d-*Camphor*-m-*nitrobenzylimide*, prepared similarly (the heating lasted 3 hours), crystallises in short, tabular columns, m. p. 69°. 0·1525 gave 11·7 c.c. N_2 (moist) at 741 mm. and 15·8°. N = 8·80 ($C_{17}H_{21}O_4N_2$ requires N = 8·86 per cent.).

d-*Benzylcamphoramic Acid*, $CO_2H{\cdot}C_8H_{14}{\cdot}CO{\cdot}NH{\cdot}C_7H_7$. — An alcoholic solution of *d*-camphorbenzylimide containing excess of potassium hydroxide was boiled for 10 hours, cooled, acidified with hydrochloric acid, and the alcohol evaporated. The residue was well washed with water, and crystallised from dilute alcohol in short, colourless, rectangular needles, m. p. 149°. 0·3340 required 12·6 c.c. of *N*/10·86-NaOH; *M* = 290 (Calc., 289). The sodium, potassium, and barium salts of the acid are colourless substances.

m-*Nitrobenzylcamphoramic Acids*.—Two forms of the acid, m. p. 134° and 179°, colourless substances with a faint green tinge, were prepared by the hydrolysis of *d*-camphor-*m*-nitrobenzylimide with potassium hydroxide solution. They were separated by fractional crystallisation from dilute alcohol, the compound of higher melting point separating first. The other compound was obtained only in a very small quantity; its properties were therefore not studied. 0·0558 (m. p. 134°) required 18 c.c. *N*/108·6-NaOH; *M* = 333. 0·2890 (m. p. 179°) required 9·35 c.c. *N*/10·86-NaOH; *M* = 336 (Calc., 335).

p-*Nitrobenzyl*-d-*camphoramic Acids*.—Two forms were prepared by hydrolysing *d*-camphor-*p*-nitrobenzylimide, namely, a brown-orange form decomposing at about 250°, and a deep purple-brown variety, which does not melt even at 325°. They yield sodium, potassium, and barium salts as brown substances. The deep purple variety was analysed: 0·1000 gave 0·2200 CO_2 and 0·0617 H_2O. C = 60·0; H = 6·85 ($C_{17}H_{22}O_5N_2$ requires C = 61·1; H = 6·6 per cent.).

o-*Nitrobenzyl*-d-*camphoramic Acid*.—By hydrolysing *d*-camphor-o-nitrobenzylimide with potassium hydroxide solution, and fractionating from hot alcohol, two varieties, one dark greenish-brown and the other brown, were obtained. They gave no definite melting points, but decomposed on heating. The brown variety was analysed: 0·1020 gave 0·2222 CO_2 and 0·0587 H_2O. C = 59·4; H = 6·3 per cent. The sodium, potassium, and barium salts are brown.

Solvent.	Concentration. g./100 c.c.	Temp.	Molecular rotatory powers. $[M]_{5893}$.	$[M]_{5780}$.	$[M]_{5461}$.	Dispersion-ratio $\frac{\alpha_{5461}}{\alpha_{5893}}$.
			d-*Camphorimide.*			
Chloroform ...	1·807	18·5°	+12·3°	+12·6°	+14·3°	1·16
Benzene	2·453	15·0	1·5	1·8	3·2	2·05
Acetone	2·315	15·0	5·1	5·5	8·7	1·72
Ether	3·363	18·0	5·2	5·6	7·2	1·38
Ethyl alcohol ...	1·591	18·0	11·0	12·3	17·1	1·55
Methyl alcohol	1·748	18·0	9·8	10·6	12·9	1·32
			d-*Camphorbenzylimide.*			
Chloroform ...	2·366	18·5°	+28·6°	+29·8°	+35·0°	1·22
Benzene	1·854	15·0	16·8	17·5	23·7	1·44
Acetone.	1·711	15·0	34·0	35·0	39·5	1·16
Ether	2·030	18·0	27·6	28·6	33·8	1·24
Ethyl alcohol ...	1·881	18·0	30·2	31·7	38·1	1·26
Methyl alcohol	1·478	18·0	24·6	26·5	35·2*	1·44
			d-*Camphor*-o-*nitrobenzylimide.*			
Chloroform ...	2·637	18·5°	+19·8°	+21·0°	+26·7°	1·36
Benzene	2·266	15·0	50·4	51·5	57·4	1·14
Acetone	2·000	15·0	42·7	44·2	54·5	1·30
Ether	1·729	18·0	40·4	42·4	49·3	1·23
Ethyl alcohol ...	0·859	27·0	40·4	—	—	—
Methyl alcohol	1·257	27·0	31·4	—	—	—
			d-*Camphor*-m-*nitrobenzylimide.*			
Chloroform ...	1·600	18·5°	+35·1°	+36·3°	+46·1°	1·31
Benzene	1·892	15·0	15·9	17·0	22·8	1·44
Acetone	2·048	15·0	39·6	40·7	45·5	1·17
Ether	2·377	18·0	34·6	35·9	42·9	1·23
Ethyl alcohol ...	1·738	18·0	31·9	33·6	41·8	1·31
Methyl alcohol	0·925	26·0	37·6	—	—	—
			d-*Camphor*-p-*nitrobenzylimide.*			
Chloroform ...	1·899	18·5°	+38·9°	+40·3°	+49·9°	1·23
Benzene	1·973	26·0	14·4	—	—	—
Acetone	1·822	15·0	41·6	42·7	52·3	1·27
Ether	1·949	18·0	27·8	28·4	31·0	1·13
Ethyl alcohol ...	0·676	18·0	36·4	37·5	53·9	1·48
Methyl alcohol	0·344	18·0	41·3	47·7	64·3	1·56

The rotatory powers of the above compounds were determined by dissolving a given weight of the substance in a solvent and making up the solution to a definite volume. The readings were taken in a 2 dcm. tube within an hour of making up the solution. The observed rotations were multiplied by a factor of about 50 in order to convert them into molecular rotations, which are therefore only correct to about half a degree.

We wish to thank Babu Indramani Mahanti, B.Sc., for checking a few of the determinations.

RAVENSHAW COLLEGE, CUTTACK,
ORISSA, INDIA.

[*Received, April 12th*, 1924.]

CCXL.—*The Hydrolysis of the* p-*Toluenesulphonchloroamides in Water.*

By FREDERICK GEORGE SOPER.

THE hydrolysis of chloroamines in aqueous solution to amine and hypochlorous acid, $:NCl + H_2O \rightleftharpoons HClO + :NH$, was first demonstrated by Orton and Gray (*Rep. Brit. Assoc.*, 1913, p. 136), but up to the present no quantitative study of such hydrolyses has been made. The hydrolysis into hypochlorous acid is definite proof of the positive nature of the chlorine in nitrogen chlorides (Selivanov, *Ber.*, 1892, **25**, 3617), and the magnitude of the hydrolysis constants will probably be connected with the polarity of the nitrogen atom, which is affected by the presence and vicinity of various groups.

The equilibrium $:NCl + H_2O \rightleftharpoons HClO + :NH$ does not lend itself to investigation by the methods based on electrical conductivity, distribution between two phases, or on cryoscopic measurements, and a method based on the solubility of a standard chloroamine of known hydrolysis constant in solutions of the particular amines has been devised (compare Lowenherz, *Z. physikal. Chem.*, 1898, **25**, 385). *p*-Toluenesulphondichloroamide was selected after numerous trials as the standard chloroamine for this purpose, as its rate of hydrolysis into hypochlorous acid was found to be rapid, which is essential if equilibrium with solutions of amines is to be attained sufficiently quickly. Further its non-reactivity with chlorine to form *C*-chlorinated derivatives considerably simplifies the determination of its hydrolysis constants.

In the present paper an account is given of the investigation of the equilibria

$$C_7H_7\cdot SO_2\cdot NCl_2 + H_2O \rightleftharpoons C_7H_7\cdot SO_2\cdot NHCl + HClO.$$
$$C_7H_7\cdot SO_2\cdot NHCl + H_2O \rightleftharpoons C_7H_7\cdot SO_2\cdot NH_2 + HClO.$$

It has not been possible to isolate the *p*-toluenesulphonmonochloroamide, for on acidifying its sodium derivative, chloramine-T, the dichloroamide is precipitated, arising probably from interaction of unhydrolysed monochloride with its hydrolysis product (Chattaway, J., 1905, **87**, 145).

That *p*-toluenesulphonmonochloroamide exists in solution is apparent from the following considerations. The solubility of the dichloroamide in water, as measured by the thiosulphate titre of its saturated solution after addition to acidified potassium iodide, is made up of the concentrations of unhydrolysed dichloroamide, hypochlorous acid, and possibly the monochloroamide. If

p-toluenesulphondichloroamide hydrolyses in water directly to the sulphonamide, $C_7H_7{\cdot}SO_2{\cdot}NCl_2 + 2H_2O \rightleftharpoons C_7H_7{\cdot}SO_2{\cdot}NH_2 + 2HClO$, the solubility of the dichloroamide should be less in solutions of the sulphonamide than in pure water. The reverse is the case. Whereas the aqueous saturated solution at 25° is 0·6720 millinormal, in a 2 millimolar solution of the sulphonamide it becomes 2·93 millinormal. This apparent increased solubility can only be due to the formation of the monochloroamide in solution, partly by combination of the hypochlorous acid with the added sulphonamide, and partly by hydrolysis of the *p*-toluenesulphondichloroamide.

The presence of hypochlorous acid in solution can be proved by distillation under reduced pressure (Orton and Gray, *loc. cit.*), and its existence as one of the equilibrants is confirmed by the action of hypochlorous acid on the sulphonamide, a sharp separation of the dichloroamide resulting when a certain concentration of hypochlorous acid is attained.

The monochloroamide probably exists as an equilibrium mixture of two isomerides, $C_7H_7{\cdot}SO_2{\cdot}NHCl$ and $C_7H_7{\cdot}SO_2H{:}NCl$, of the latter of which, chloramine-T is the sodium salt. In the following investigation the concentration of the monochloroamide has been taken as the sum of the concentrations of the isomerides, a procedure which appeared justifiable since the hydrolysis of the monochloroamide prepared by mixture of equimolecular quantities of the sulphonamide and hypochlorous acid was identical with that of the monochloroamide obtained by acidifying chloramine-T. It was thus evident that equilibrium between the two isomerides is rapidly attained, so that the ratio of one form to the other in solution is constant under the same conditions of temperature and medium, *i.e.*, the active mass of either is proportional to the sum of their concentrations.

Owing to the sparing solubility of the dichloroamide in water, and, as is shown later, its slight hydrolysis, a direct determination of the concentration of any one of the equilibrants was not possible by phase partition methods. Further, the estimation of hypochlorous acid by a conductivity method was precluded owing to its weak acidic character.

The hydrolysis constants have consequently been calculated by combining two series of independent experimental data, (a) estimations of the solubility of the dichloroamide in solutions of the sulphonamide, and (b) determinations of the free chlorine in solutions of chloramine-T acidified with hydrochloric acid.

Consideration of (a).—The thiosulphate titre of a saturated solution of the dichloroamide is a measure of the sum of the con-

centrations of unhydrolysed dichloroamide, the monochloroamide, hypochlorous acid, and their ions. The ions may be eliminated by dissolving the dichloroamide in weak solutions of a strong acid. The repression of ionisation causes a lowering of the apparent solubility, owing to the disappearance of the hypochlorite-ion, ClO′. The minimum apparent solubility corresponding with complete repression of ionisation is observed in $N/500$-sulphuric acid. In the determination of the apparent solubility of the dichloroamide in solutions of the sulphonamide, an identical concentration of acid was maintained, so that the titre measured the concentrations of the unhydrolysed dichloroamide (a constant quantity in the presence of the solid phase), the monochloroamide, and un-ionised hypochlorous acid.

If T_1 is the thiosulphate titre, expressed as milli-equivalents of titrable hypochlorous acid per litre, of the saturated solution of the dichloroamide, c that of the unhydrolysed dichloroamide, b_0 that of the monochloroamide, and f_0 that of the hypochlorous acid, c, b_0, and f_0 being in millimols. per litre,

$$T_1 = 4c + 2b_0 + 2f_0 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The further hydrolysis of the monochloroamide into sulphonamide and hypochlorous acid in presence of an equivalent amount of hypochlorous acid is very slight (see below), and it is sufficiently accurate to take b_0 as sensibly equal to f_0 in aqueous solution. Equation (1) then reduces to $T_1 = 4c + 4f_0$.

If T_2 is the titre of the saturated solution in a solution of the sulphonamide of p millimols./litre, a and b the concentrations of free sulphonamide and monochloroamide, respectively,

$$b = (T_2 - 4c - [\mathrm{HClO}])/2 = (T_2 - 4c)/2 \quad . \quad . \quad (2)$$

since, as is shown later, the concentration of the hypochlorous acid is negligibly small.

Since only half of the sulphonmonochloroamide has been formed from the sulphonamide initially present, the concentration of free sulphonamide is given by the equation

$$a = p - (T_2 - 4c)/4 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If K_1 and K_2 are the primary and secondary hydrolysis constants

$$K_1 = [\mathrm{C_7H_7{\cdot}SO_2{\cdot}NHCl}][\mathrm{HClO}]/[\mathrm{C_7H_7{\cdot}SO_2{\cdot}NCl_2}] = b[\mathrm{HClO}]/c \quad (4)$$

$$K_2 = [\mathrm{C_7H_7{\cdot}SO_2{\cdot}NH_2}][\mathrm{HClO}]/[\mathrm{C_7H_7{\cdot}SO_2{\cdot}NHCl}] = a[\mathrm{HClO}]/b \quad (5)$$

Eliminating [HClO],

$$K_1 = b^2/ac \,.\, K_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Estimation of the true solubility of unhydrolysed dichloroamide in water.—When the dichloroamide is dissolved in solutions of hypochlorous acid, the hydrolysis of the dichloroamide is forced back. The increase in the thiosulphate titre of the hypochlorous acid due to solution of the dichloroamide will, in the presence of excess of this acid, measure the solubility of the unhydrolysed dichloroamide ($= c$). The solubility measured in this way was not further decreased by increase of the hypochlorous acid concentration beyond $M/1000$. The diminution in the solubility was, however, not sufficiently great to allow of the estimation of b_0 and f_0 from equation (1).

Consideration of (b).—This relation (6) is then combined with data obtained from the determination, by an aspiration method, of the free chlorine in solutions of chloramine-T acidified with hydrochloric acid (Orton and Jones, J., 1909, **95**, 1456).

$$C_7H_7\cdot SO_2\cdot NHCl \qquad HCl$$
$$C_7H_7\cdot SO_2\cdot NCl_2 \quad \uparrow\downarrow \quad + HClO \rightleftharpoons Cl_2$$
$$C_7H_7\cdot SO_2\cdot NH_2$$

Solutions of chlorine in hydrochloric acid are first examined by slowly aspirating a known volume of air through the mixture at 25°, and absorption of the removed chlorine by potassium iodide. This determines the distribution ratio of chlorine between air and hydrochloric acid. Hydrochloric acid solutions of chloramine-T of less than 1 millimol./litre in order to prevent precipitation of the dichloroamide, are similarly treated and the concentration of free chlorine deduced from that of the chlorine in the air after aspiration through the solution. The concentration of free chlorine is found to be the same when equimolecular mixtures of the monochloroamide and hypochlorous acid are employed instead of chloramine-T.

If g is the concentration of free chlorine in the solution, f the concentration of hypochlorous acid calculated from the hydrolysis constant of chlorine (Jakowkin, *Z. physikal. Chem.*, 1899, **29**, 613), T_3 the titre of the solution in millinormal units, d the concentration of free monochloroamide, and e that of the dichloroamide,

$$d + 2e + g + f = T_3/2 = h \quad . \quad . \quad . \quad . \quad (7)$$

$d = h - (2e + g)$, neglecting the small term f, and from the general conditions of equilibrium

$$[C_7H_7\cdot SO_2\cdot NH_2] = [HClO] + [Cl_2] + [C_7H_7\cdot SO_2\cdot NCl_2] = g + e \quad (8)$$

since the [HClO] is negligible.

Substituting for K_2,

$$K_2 = [C_7H_7{\cdot}SO_2{\cdot}NH_2][HClO]/[C_7H_7{\cdot}SO_2{\cdot}NHCl]$$
$$= f(g + e)/(h - 2e - g) \quad . \quad . \quad . \quad . \quad (9)$$

and from (6),

$$K_2 = (ac/b^2)K_1 = acf(h - 2e \quad g)/eb^2 \quad . \quad . \quad (10)$$

Equations (9) and (10) reduce to a quadratic in e:

$$e^2(b^2/ac - 4) + e\{b^2g/ac + 4(h - g)\} - (h - g)^2 = 0 \quad . \quad . \quad (11)$$

which allows of the calculation of e and hence of K_1 and K_2.

Results.

In Table I is given the solubility of the dichloroamide in water and in aqueous sulphuric acid at 25·0°.

TABLE I.

Conc. of H_2SO_4	0	1·00	2·00	5·00 $N \times 10^{-3}$
Titre of solution	0·347	0·343	0·342	0·342 $N \times 10^{-3}$

Substituting in (1), $4c + 4f_0 = 0{\cdot}342\ N \times 10^{-3}$.

In Table II is given the solubility of the dichloroamide in aqueous hypochlorous acid.

TABLE II.

Titre of 500 c.c. of HClO soln. in 0·7929N/100-thio.	85·234	104·02	259·50 c.c.
Total titre of 500 c.c. after satn. with $C_7H_7{\cdot}SO_2{\cdot}NCl_2$	104·35	122·88	278·42 c.c.
Titre due to dichloroamide	19·12	18·86	18·92 c.c.
	=0·303	0·299	0·300 $N \times 10^{-3}$

This value for c is rather lower than that found by successive approximation on equations 6, 11, 9, and 10, which is 0·310 $N \times 10^{-3}$. This is doubtless due to slight decomposition of the hypochlorous acid during the experiment.

In Table III are given the apparent solubilities of the dichloroamide in solutions of the sulphonamide.

TABLE III.

Conc. of sulphonamide.	Titre of solution.	b.	a.	b^2/ac.
0·5 $N \times 10^{-3}$	1·414 $N \times 10^{-3}$	1·104 $M \times 10^{-3}$	0·224 $M \times 10^{-3}$	17·3
1·0	2·021	0·855	0·573	16·24
2·0	2·949	1·319	1·341	16·5
5·0	4·704	2·197	3·902	15·74
6·5	5·496	2·593	5·204	16·44
8·0	6·134	2·912	6·544	16·5
10·0	6·870	3·280	8·360	16·4
		Mean (neglecting the first value)		16·3

Table IV gives the results obtained by the slow aspiration of air through solutions of chlorine in 0·25 *N*-, 0·5 *N*-, and 1·0*N*-hydrochloric acid at 25·0°.

TABLE IV.

Titre of 200 c.c. of air in c.c. of *N*/500-thio.	Titre of 200 c.c. of Cl_2 solution.	$C_{air}/C_{solution}$.	Titre of 200 c.c. of air in c.c. of *N*/500-thio.	Titre of 200 c.c. of Cl_2 solution.	$C_{air}/C_{solution}$.
		0·25*N*-Hydrochloric acid.			
9·40	35·68	0·263	4·34	15·89	0·273
15·90	57·00	0·279	13·76	51·12	0·269
20·43	75·40	0·271		Mean	0·271
		0·5*N*-Hydrochloric acid.			
11·26	41·23	0·273	2·73	10·12	0·270
				Mean	0·271
		1·0*N*-Hydrochloric acid.			
14·54	51·47	0·266	6·10	22·35	0·273
8·82	32·87	0·268	4·14	15·38	0·269
				Mean	0·269

Table V is obtained from the aspiration of chlorine from solutions of chloramine-T in hydrochloric acid at the above concentrations.

TABLE V.

0·25*N*-Hydrochloric acid ($\gamma = 0·770$).

Expt.	1	2	3	4
Titre of 1 litre of air in c.c. of *N*/500-thio.	5·46	4·34	4·34	3·79
$g = [Cl_2]$	0·02014	0·016	0·016	0·014 $M \times 10^{-3}$
$f \times 10^4 = [HClO]$	2·445	1·94	1·94	1·70 $M \times 10^{-3}$
$h = T_3/2$	1·013	0·359	0·617	0·523 $N \times 10^{-3}/2$

0·5*N*-Hydrochloric acid ($\gamma = 0·762$).

Expt.	5	6	7	8
Titre of 1 litre of air in c.c. of *N*/500-thio.	14·05	10·26	13·76	12·42
g	0·052	0·038	0·051	0·046 $M \times 10^{-3}$
$f \times 10^4$	1·612	1·18	1·582	1·43 $M \times 10^{-3}$
h	1·001	0·423	0·822	0·631 $N \times 10^{-3}/2$

1·0*N*-Hydrochloric acid ($\gamma = 0·823$).

Expt.	9	10	11	12
Titre of 500 c.c. of air in c.c. of *N*/500-thio.	23·95	16·74	20·98	15·88
g	0·1781	0·1244	0·156	0·108 $M \times 10^{-3}$
$f \times 10^4$	1·184	0·825	1·036	0·717 $M \times 10^{-3}$
h	0·859	0·459	0·691	0·342 $N \times 10^{-3}/2$

The concentrations of hypochlorous acid in the above table have been calculated from the expression $[HClO] \cdot \gamma^2[HCl]^2/[Cl]_2 = 450$ at 25°, in which the concentration of the hydrochloric acid is in

milliequivalents, and γ is the activity coefficient as determined by Lewis and Randall (*J. Amer. Chem. Soc.*, 1921, **43**, 1112).

Substituting for g and h and the mean value for b^2/ac in equation (2), one obtains as values for e:

TABLE VI.

Expt.		e in $M \times 10^{-3}$	$K_2 \times 10^8$ mols.
1	$12{\cdot}3e^2 + 4{\cdot}30e - 0{\cdot}986 = 0$	0·1576	6·4
2	$12{\cdot}3e^2 + 1{\cdot}633e - 0{\cdot}1176 = 0$	0·0514	5·42
3	$12{\cdot}3e^2 + 2{\cdot}664e - 0{\cdot}3612 = 0$	0·0984	5·47
4	$12{\cdot}3e^2 + 2{\cdot}264e - 0{\cdot}2591 = 0$	0·0798	4·76
5	$12{\cdot}3e^2 + 4{\cdot}644e - 0{\cdot}9006 = 0$	0·1412	4·67
6	$12{\cdot}3e^2 + 1{\cdot}716e - 0{\cdot}07508 = 0$	0·0350	4·22
7	$12{\cdot}3e^2 + 3{\cdot}915e - 0{\cdot}5944 = 0$	0·1122	4·71
8	$12{\cdot}3e^2 + 3{\cdot}089e - 0{\cdot}3422 = 0$	0·0833	4·41
9	$12{\cdot}3e^2 + 5{\cdot}620e - 0{\cdot}4638 = 0$	0·0715	5·49
10	$12{\cdot}3e^2 + 3{\cdot}370e - 0{\cdot}1122 = 0$	0·0301	4·63
11	$12{\cdot}3e^2 + 4{\cdot}680e - 0{\cdot}2862 = 0$	0·0536	5·08
12	$12{\cdot}3e^2 + 2{\cdot}700e - 0{\cdot}0548 = 0$	0·0187	4·62

Experiments (3) and (10) were made on the monochloroamide prepared by mixing equimolecular quantities of hypochlorous acid and sulphonamide. The others were made on acidified chloramine-T solution.

Mean value of K_2, omitting the value 6·4, is $4{\cdot}9 \times 10^{-8}$; the corresponding value of $K_1 = b^2/ac \,.\, K_2 = 8{\cdot}0 \times 10^{-7}$.

Solubility of the Dichloroamide in Hydrochloric Acid.—The accuracy of the values of the hydrolysis constants was then tested by the determination of the apparent solubility of the dichloroamide in solutions of hydrochloric acid of varying strength.

The apparent observed solubility is made up of the concentration of dichloroamide (which is apparently constant, unlike that of an electrolyte [Noyes and Bray, *J. Amer. Chem. Soc.*, 1911, **33**, 1643]) and those of the chlorine and monochloroamide. The concentration of the hypochlorous acid is neglected, as in 0·3*N*-hydrochloric acid the ratio of $[HClO]/[Cl_2]$ is 0·8 per cent. and decreases with further addition of hydrochloric acid. The constant true solubility of unhydrolysed *p*-toluenesulphondichloroamide on which the validity of the method depends was shown by the study of its solubility in aqueous sulphuric acid. No diminution in the titre of the saturated solution at 25°, beyond that occurring in *N*/500-sulphuric acid due to repression of ionisation, was observed in sulphuric acid at concentrations ranging up to *N*. The tendency was, in fact, to obtain a slightly enhanced value of the apparent solubility, due probably to decomposition of the hypochlorous acid and consequent further solution and hydrolysis of the dichloroamide, with the resulting accumulation of the monochloroamide in the system.

Calculation of the Solubility.—The concentrations of the equilibrants are determined by equations (7) and (5), whilst (4) reduces to

$$[C_7H_7\cdot SO_2\cdot NHCl][HClO] = 8\cdot0 \times 10^{-4}[C_7H_7\cdot SO_2\cdot NCl_2] = 6\cdot27 \times 10^{-5} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

and from the general conditions of equilibrium,

$$[Cl_2] - [C_7H_7\cdot SO_2\cdot NHCl] = [C_7H_7\cdot SO_2\cdot NH_2] \quad . \quad (13)$$

These equations reduce to a cubic equation in [HClO]:

$$\{[\gamma HCl]^2/450\}[HClO]^3 - 6\cdot27 \times 10^{-3}[HClO] - 6\cdot27 \times 10^{-5} = 0 \quad (14)$$

This allows of the calculation of [HClO] by Horner's method and hence of $[Cl_2]$ and the monochloroamide. Table VII gives the calculated and observed values.

TABLE VII.

Conc. of HCl	1·0	0·7	0·5	0·3 *N*
Titre of soln. (found)	1·54	1·072	0·817	0·765 $N \times 10^{-3}$
Calculated titre	1·57	1·15	0·88	0·77 $N \times 10^{-3}$

Special precautions were taken in these experiments to avoid escape of the chlorine during the preparation of the system.

Calculation of the Composition of Acidified Chloramine-T.—In solutions of chloramine-T acidified with a mineral acid other than hydrochloric acid, one may assume that the sodium is completely displaced from the *p*-toluenesulphonchloroamide with the production of free mono- and di-chloroamides, the amounts of which may be calculated.

If A is the initial concentration ($M \times 10^{-3}$) of the chloramine-T, it follows that

$$2[C_7H_7\cdot SO_2\cdot NCl_2] + [C_7H_7\cdot SO_2\cdot NHCl] + [HClO] = A \quad . \quad . \quad (15)$$

$$[C_7H_7\cdot SO_2\cdot NCl_2] + [HClO] = [C_7H_7\cdot SO_2\cdot NH_2] \quad . \quad . \quad . \quad . \quad (16)$$

Combining these equations with (4) and (5), one obtains

$$[HClO] + [C_7H_7\cdot SO_2\cdot NCl_2] = [C_7H_7\cdot SO_2\cdot NHCl]K_2 \quad . \quad (17)$$

by neglecting the term in $[HClO]^2$, and therefore

$$[C_7H_7\cdot SO_2\cdot NCl_2] = [C_7H_7\cdot SO_2\cdot NHCl]\sqrt{K_2/K_1} \quad . \quad . \quad . \quad . \quad (18)$$

$$[HClO] = K_1[C_7H_7\cdot SO_2\cdot NCl_2]/[C_7H_7\cdot SO_2\cdot NHCl] = \sqrt{K_1K_2} = 2 \times 10^{-4}\ M \times 10^{-3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

$$2[C_7H_7\cdot SO_2\cdot NCl_2] + [C_7H_7\cdot SO_2\cdot NHCl] = A - 0\cdot0002 \quad . \quad . \quad (20)$$

$$\text{or } 1\cdot495\ [C_7H_7\cdot SO_2\cdot NHCl] = A - 0\cdot0002 \quad . \quad . \quad . \quad . \quad . \quad (21)$$

The calculated values of the equilibrium concentrations in acidified chloramine-T solutions are given in Table VIII.

TABLE VIII.

Titre of solution	2·0	1·0	0·6	0·2 $N \times 10^{-3}$
$C_7H_7 \cdot SO_2 \cdot NHCl$	0·669	0·334	0·201	0·067 $M \times 10^{-3}$
$C_7H_7 \cdot SO_2 \cdot NCl_2$	0·165	0·083	0·050	0·016 $M \times 10^{-3}$
$C_7H_7 \cdot SO_2 \cdot NH_2$	0·0002	0·0002	0·0002	0·0002 $M \times 10^{-3}$

The composition of alkaline solutions of chloramine-T has not yet been calculated. Preliminary values for the hydrolysis of the sodium salt and hence of the acidic strength of *p*-toluenesulphonmonochloroamide have been obtained. Whilst the combination of the sodium hydroxide with the monochloroamide is rapid (so that a state of equilibrium is rapidly attained), that of the base and *p*-toluenesulphonamide is comparatively slow; for, when the dichloroamide is added to a solution of sodium hydroxide, the thiosulphate titre of the solution rapidly reaches a maximum. This is due to the formation of sodium hypochlorite and chloramine-T. The titre of the solution then falls and the sulphondichloroamide is again precipitated owing to the liberation of hypochlorous acid and monochloroamide from their sodium salts, the sodium forming sodium sulphonamide. This work is now in progress.

EXPERIMENTAL.

Purity of Water.—For all the foregoing work water of a specially high degree of purity was essential (compare Orton and Gray, *loc. cit.*). The water used, distilled from alkaline potassium permanganate solution, was of conductivity grade. To test the stability of hypochlorous acid in this water, the titre of a hypochlorous acid solution was observed over a period of 14 days. No appreciable fall in titre was observed. The solution was contained in a well-stoppered flask, blackened with Brunswick Black.

Time.	0	1	3	7	14 days.
Titre of 25 c.c.	24·72	24·70	24·78	24·74	24·75 c.c. of N/500-thio.

Stability of a Solution of the p-*Toluenesulphonchloroamides in Water.*—The stability of chloroacetanilide in specially purified water has been extensively studied by Orton and Gray (*loc. cit.*), who drew the conclusion that the fall in titre was due to a hydrolysis of the free anilide to aniline, which was then rapidly oxidised by the hypochlorous acid. A solution of *p*-toluenesulphonchloroamide in water was found to be quite stable over 14 days. The solution examined was an aqueous sulphuric acid solution of chloramine-T.

Time.	0	1	5	7	14 days.
Titre of 25 c.c.	14·39	14·38	14·39	14·40	14·37 c.c. of N/500-thio

With ordinary distilled water there is, however, an appreciable decomposition in 7 days.

Time.	0	1	2	7 days.
Titre of 25 c.c.	12·13	11·79	11·51	10·07 c.c. of N/500-thio.

The Titration of Hypochlorous Acid and Chloroamide Solutions.—The iodine liberated by the hypochlorous acid from acidified potassium iodide was titrated with sodium thiosulphate solution. As the concentration of the iodine was in some cases very small, sodium thiosulphate of a higher dilution than commonly used had to be employed. To avoid the recurrence of the blue colour of the starch-iodine complex at the end-point, which is particularly troublesome with dilute ($<N/200$) sodium thiosulphate, sodium acetate solution was added to destroy the free hydriodic acid, the oxidation of which by oxygen in solution is the probable cause of this loss of sharpness in titration. Still better results were obtained if the oxygen in solution was removed by bubbling a stream of nitrogen through the solution to be titrated for about 1 minute. When larger volumes of liquid had to be titrated (more than 100 c.c.), the liquid was contained in a glass cylinder standing on a porcelain plate, and a mirror set at 45° reflected the column of liquid, which was conveniently stirred by a current of nitrogen. It was found that the addition of one drop of N/500-thiosulphate solution to 400 c.c. effected a sharp discoloration of the starch-iodine solution.

Determination of the Solubility.—The chloroamide and the aqueous solution in which the apparent solubility was being determined were placed in a glass stoppered bottle, fixed in a rotating frame in a thermostat regulated to $25{\cdot}0° \pm 0{\cdot}1°$. Saturation was complete in from 3 to 6 hours. The solution was filtered by insertion of a tube of wide bore, over the end of which had been fused a piece of perforated platinum foil. This perforated plate supported a piece of filter paper secured by a silver wire. The solution was forced up this tube by air pressure, and a quantity removed by a pipette.

The Aspiration of Chlorine from its Solutions.—The apparatus was similar to that used by Jones (J., 1911, **99**, 392), with an addition that has been found advantageous. The air was drawn through the chlorine solution in a wash-bottle A (volume 1360 c.c.) and through the potassium iodide solutions in wash-bottles B and C by connexion with an aspirator D. The volume of air drawn through the solution was measured by the volume of water (collected in a flask E) delivered by the aspirator. To overcome the difficulties introduced by the variation of pressure of the air inside the aspirator due to the suction of air against hydrostatic pressure in the wash-

bottles A, B, and C, air was partly forced through by connecting A with the measuring flask, E. The pressure in the aspirator D, as shown by an attached water-manometer, remained constant throughout the experiment. The time occupied by the aspiration of 200 c.c. of air was approximately 2 hours. Increase of the time to 3 hours had no effect on the chlorine concentration of the gas phase. To prevent spray from the chlorine solution being carried over with the mixture of air and chlorine, a plug of glass wool was placed in the tube connecting A and B.

Procedure.—5·851 *N*-Hydrochloric acid (232·8 c.c.) was diluted nearly to 1360 c.c. (the volume of A, so that the concentration of the hydrochloric acid was normal), allowed to come to thermal equilibrium at 25°, and the requisite amount of hypochlorous acid solution added to give chlorine solutions ranging from 0·01 to 1 millimolar. These solutions were titrated immediately after the aspiration in every case. The slight amounts of chlorine withdrawn from the large volume of mixture caused no appreciable fall in the titre.

Preparation and Purification of Materials.—Hypochlorous acid. Equivalent quantities of bleaching powder and boric acid were distilled under diminished pressure. The distillate was freed from traces of chlorine by redistillation from yellow mercuric oxide and kept in a well-blackened bottle.

Chloramine-T. This salt crystallises with 3 mols. of water. It was recrystallised from dilute aqueous sodium hydroxide, washed with a small quantity of water, and the product dried for 36 hours over potassium carbonate (Found: available Cl = 12·38. Calc., Cl = 12·59 per cent.).

p-Toluenesulphondichloroamide was prepared by the addition of excess (10 per cent.) of bleaching powder solution to 10 gms. of the sulphonamide in 150 c.c. of glacial acetic acid. The dichloroamide, which was immediately precipitated as a fine powder, was washed with water by shaking (4—5 times) in a large stoppered bottle at 25° until the titre of the saturated solution was constant. This ensured the complete removal of traces of the sulphonamide (which obviously must be absent, otherwise the apparent solubility would be too great).

p-Toluenesulphonamide was recrystallised from acetic acid, thereby avoiding the formation of the monohydrate. M. p. 137°.

Hydrochloric acid. The constant-boiling mixture was distilled from an all-glass distillation apparatus. Its normality, determined by gravimetric analysis, was 5·851.

Summary.

1. Toluenesulphondichloroamide hydrolyses in water into hypochlorous acid and the monochloroamide, which though not isolated has been shown to exist in solution.

2. The equilibrium constants of the hydrolysis of the mono- and di-chloroamides of *p*-toluenesulphonamide in water at 25° are $4{\cdot}9 \times 10^{-8}$ and $8{\cdot}0 \times 10^{-7}$, respectively.

3. The accuracy of the values of these hydrolysis constants has been tested by the determination of the solubility of the dichloroamide in hydrochloric acid.

4. The composition of acidified chloramine-T solutions has been calculated. It is shown that the concentration of hypochlorous acid in such solutions is independent of the concentration of the chloramine-T.

My best thanks are due to Professor K. J. P. Orton, F.R.S., who suggested the investigation of the hydrolysis of chloroamines in water, for his valuable criticisms and suggestions.

UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR

[*Received, May 30th,* 1924.]

CCXLI.—*Compounds of Tervalent Molybdenum. Part I. A New Oxysulphate.*

By WILLIAM WARDLAW, FRANK HAROLD NICHOLLS, and NORMAN DARBY SYLVESTER.

MOLYBDENUM, tungsten, and uranium, in their highest stage of oxidation, form together with chromium a group of closely related elements, but much yet remains to be discovered concerning their tervalent derivatives. Although complex salts of the types $[MoCl_6]R_3$, $[MoCl_5H_2O]R_2$, $[MoBr_5H_2O]R_2$, $Mo_2F_9R_3$, and $[Mo(CNS)_6]R_3$ have been isolated, the chloride, bromide, and sulphide are the only simple salts of tervalent molybdenum known. Attempts to prepare the alums and oxalates (Foerster and Fricke, *J. angew. Chem.*, 1923, **36**, 62, 458; Chilesotti, *Z. Elektrochem.*, 1906, **12**, 146, 173) have been unsuccessful.

Early investigators endeavoured to isolate tervalent salts of molybdenum by evaporating reduced solutions of the trioxide, and obtained grey or greyish-black residues which were apparently the products of hydrolysis and oxidation of the compounds sought.

By taking suitable precautions, we have been able to isolate from a solution of molybdenum trioxide in sulphuric acid reduced to the tervalent state, a well-defined *hydrated molybdenum oxysulphate*, $Mo_2O(SO_4)_2,xH_2O$, where x is 5 or 6.

Experimental.

Preparation of the Oxysulphate.—Molybdenum trioxide (40 gms.) was dissolved in 81 c.c. of boiling sulphuric acid (d 1·84) containing a few drops of concentrated nitric acid; the solution was made up to a litre (concentration of sulphate approximately 3N), and 500 c.c. were electrolysed in a diaphragm cell with smooth platinum electrodes (J., 1923, **123**, 969). As the final stage of reduction was approached, shown by the colour change in the cathode chamber from red to dark green, a current of air-free carbon dioxide was passed through the cell. The electrolysis was continued until the colour was vivid green. All subsequent operations were performed in atmospheres of carbon dioxide, air being rigidly excluded. The liquid was distilled under reduced pressure from an all-glass apparatus at an initial temperature of 70°, which was gradually lowered to 55° as the solution became concentrated. The whole success of this operation depends on avoiding air oxidation, and on concentrating the solution, which must be initially vivid green, to a bulk at which the colour is still distinctly green. If the temperature of distillation is too high, the solution becomes brown, and if the solution is too concentrated, the green reverts to red; from such solutions it is impossible to precipitate any solid. The green solution, after concentration and cooling, was poured into air-free acetone, and the *oxysulphate*, which separated as a fine green powder and gradually became granular, was washed with dry acetone and with dry ether and quickly transferred to a desiccator filled with carbon dioxide and containing phosphoric oxide. The substance was free from any product of hydrolysis and formed a green solution in air-free water.

Valency of the Compound.—A solution of the oxysulphate in dilute sulphuric acid was titrated in an inert atmosphere with standard permanganate solution (required: 20·25, 24·70 c.c.). A similar solution was oxidised with hydrogen peroxide, passed through the reductor (*loc. cit.*), and titrated with the permanganate (required: 20·35, 24·80 c.c.). Since the latter titration value represents the oxidation of tervalent molybdenum to the sexavalent state, it is evident that the molybdenum of the oxysulphate is tervalent.

Analysis.—The oxysulphate was oxidised by sodium peroxide and water, the excess of hydrogen peroxide removed by warming, the solution neutralised, and freshly prepared ammonium sulphide

added. The molybdenum sulphide, precipitated by hydrochloric acid, was washed with dilute hydrochloric acid (1 : 100) saturated with hydrogen sulphide, and ignited.

The sulphate in the filtrate and washings was estimated in the usual way [Found : Mo = 39·12, 37·60; Mo : SO_4 = 1 : 1, 1 : 0·95. $Mo_2O(SO_4)_2,5H_2O$ requires Mo = 39·18 per cent.; $Mo_2O(SO_4)_2,6H_2O$ requires Mo = 37·80 per cent.].

The oxysulphate was heated in a current of air-free nitrogen, and the moisture estimated by absorption. With careful temperature regulation, the oxysulphate was quantitatively decomposed to molybdenum pentoxide. Further ignition of this oxide in a current of air yielded the trioxide [Found : Mo = 39·11; H_2O = 18·04. $Mo_2O(SO_4)_2,5H_2O$ requires Mo = 39·18; H_2O = 18·37 per cent. 0·1885 gave 0·1043 residue (*b*) and 0·1106 trioxide (*c*). 0·1659 gave 0·0918 residue (*b*) and 0·0971 trioxide (*c*). Ratio *b*/*c* : Found 0·943, 0·945. Calc., 0·944].

The above results are in agreement with the decomposition $Mo_2O(SO_4)_2,xH_2O = Mo_2O_5 + 2SO_2 + xH_2O$.

Properties and Reactions of the Oxysulphate.—The freshly precipitated substance is intensely green, but on drying over phosphoric oxide it gradually becomes grey and the sulphate content decreases. The substance is very hygroscopic and readily hydrolysable. It is insoluble in alcohol, ether, or acetone, but dissolves readily in water; the solution loses its green colour immediately on exposure to air, and a rusty-brown precipitate, readily soluble in acids, gradually forms. The oxysulphate immediately precipitates the metals from solutions of copper sulphate and silver nitrate at the ordinary temperature, and reduces mercuric and ferric salts to the "ous" state. On warming with sulphur or sodium sulphite, a solution of the new solid, acidified with dilute sulphuric acid, evolves hydrogen sulphide (see J., 1923, **123**, 975). Barium chloride produces no precipitate in a freshly prepared solution of the oxysulphate, but barium sulphate is thrown down on warming. Lead acetate with acetic acid gives similar results. Sodium and potassium hydroxides give green deposits. Ammonia is without action in the cold, but produces a black precipitate on warming. Potassium ferricyanide gives a deep red coloration; a similar coloration is slowly produced by potassium ferrocyanide.

Conclusion.

No normal sulphate of molybdenum has yet been prepared. A sexavalent oxysulphate, MoO_2SO_4, separates from a solution of molybdenum trioxide in concentrated sulphuric acid (*Ber.*, 1871, **4**, 14), whilst by treatment with hydrogen sulphide this solution

yields a dark green quinquevalent oxysulphate (*Compt. rend.*, 1901, **132**, 475). Chilesotti (*loc. cit.*, p. 173) concluded from potential measurements that in the electrolytic reduction of acid solutions of molybdenum trioxide the molybdenum is first completely reduced to the quinquevalent condition and that further reduction produces tervalent molybdenum without the intermediate formation of quadrivalent compounds. If so, a quinquevalent sulphate may yet be isolated from an appropriately reduced molybdenum solution, but the isolation of a quadrivalent compound will probably not be realised. The oxysulphates so far produced form an interesting series in which the ratio of molybdenum to sulphate remains constant whilst the difference in valency involves a progressive elimination of oxygen: $Mo_2O_4(SO_4)_2$, $Mo_2O_3(SO_4)_2$, $Mo_2O(SO_4)_2$.

Double salts of the tervalent oxysulphate are being prepared and investigated.

Summary.

1. A green oxysulphate, $Mo_2O(SO_4)_2,xH_2O$, where x is 5 or 6, has been prepared from a solution of molybdenum trioxide in sulphuric acid, reduced electrolytically to the tervalent state.
2. The oxysulphate is characterised by strong reducing properties.
3. On heating, it decomposes in accordance with the equation $Mo_2O(SO_4)_2,xH_2O = Mo_2O_5 + 2SO_2 + xH_2O$.
4. The sulphate radical is not precipitated by barium chloride in the cold.

The authors wish to express their thanks to the Department of Scientific and Industrial Research for a grant to one of us (N.D.S.) which has enabled this investigation to be carried out, and to the Chemical Society for a grant towards the purchase of some of the materials.

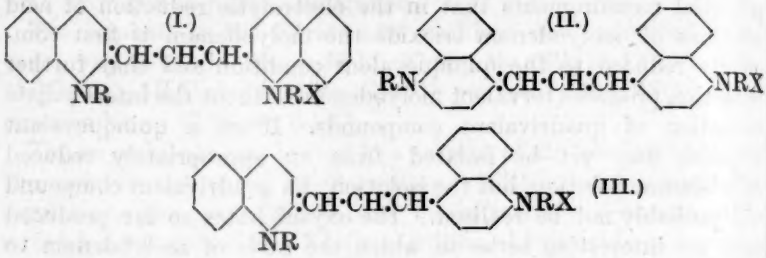
UNIVERSITY OF BIRMINGHAM. [*Received, June 26th*, 1924.]

CCXLII.—*The Cyanine Dyes. Part VIII. Synthesis of a 2 : 4′-Carbocyanine. Constitution of the Dicyanines.*

By WILLIAM HOBSON MILLS and RONALD CHARLES ODAMS.

IT was pointed out in the third paper of this series (J., 1920, **117**, 1557) that, besides the 2 : 2′-carbocyanines (I) of which pinacyanole is the chief representative, two other classes of carbocyanines con-

taining two quinoline nuclei should be capable of existence, the 4 : 4′-carbocyanines (II) and the 2 : 4′-carbocyanines (III).



A dye of the second class has recently been synthesised by W. T. K. Braunholtz and one of us (J., 1923, **123**, 2804), and has been shown to be identical with the substance kryptocyanine, prepared by Adams and Haller (*J. Amer. Chem. Soc.*, 1920, **42**, 2661).

In the present communication, the synthesis of a dye of the third class, the 2 : 4′-carbocyanines, is described.

The synthesis was effected by the method of preparing carbocyanines recently described by Mills and Braunholtz (*loc. cit.*), which consists in heating a quaternary salt of a base, such as quinaldine, lepidine, or 1-methylbenzothiazole, that contains a reactive methyl group, with di-*o*-formylmethylaminodiphenyl disulphide,

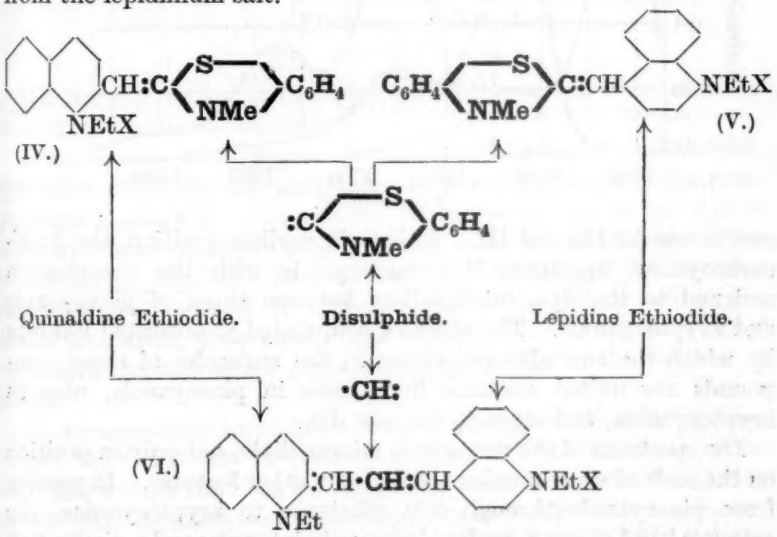
$$C_6H_4\langle^{S}_{NMe\cdot CHO}\!\!-\!\!-\!\!-

showed a brilliant green lustre and gave deep blue, alcoholic solutions decolorised by acids, and the compound acted as a powerful photographic sensitiser for the red. It had also the composition of a carbocyanine; analysis showed it to be an isomeride of pinacyanole and kryptocyanine.

It is clear that a new dye of this composition replacing to a great extent the mixture of pinacyanole and kryptocyanine which would otherwise be produced, must be formed by a carbocyanine condensation between a methenyl residue proceeding from the diformylmethylaminodiphenyl disulphide, 1 mol. of quinaldine ethonitrate, and 1 mol. of lepidine ethonitrate. The condensation of the methenyl residue therefore takes place more readily with two dissimilar molecules than with two similar molecules of the two quaternary salts.

The way in which the three chief products of the reaction are formed is indicated in the accompanying diagram, in which VI represents the new 2 : 4′-carbocyanine, IV the thio*pseudo*cyanine, and V the thio*iso*cyanine.

From analogy with the *iso*cyanines (Mills and Wishart, J., 1920, 117, 579), the acid radical in the 2 : 4′-carbocyanine is represented provisionally as associated with the half of the molecule derived from the lepidinium salt.

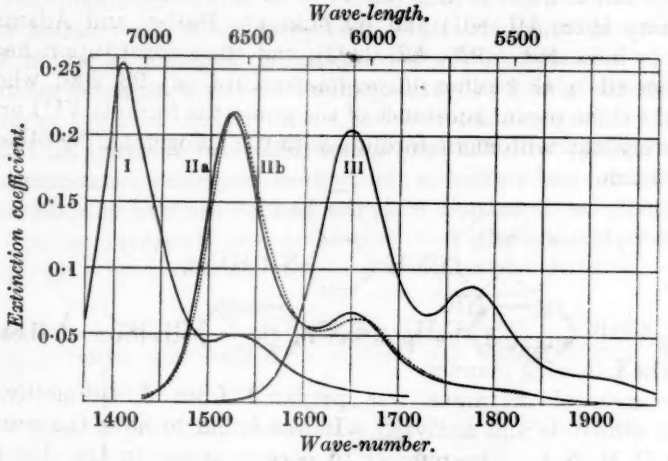


These conclusions respecting the relationship of the new carbocyanine to pinacyanole and kryptocyanine are strikingly confirmed by the absorption spectra in the visible region of the three compounds in dilute alcoholic solution. These spectra are represented in Fig. 1,

which shows the extinction coefficients of the millionth molar solutions for light of different wave-lengths plotted against the wave-number. The close relationship between the three curves, I (kryptocyanine), IIa (2 : 4′-diethylcarbocyanine iodide), and III (pinacyanole), is evident.

Each curve shows an intense primary maximum, rising more steeply on the side towards the red than on that towards the blue. At wave-numbers greater by about 125 than those corresponding with the primary maxima (the differences are 122, 127, and 130 in the three curves), there is a secondary maximum of much lower intensity, and at still higher frequencies (difference of wave-number 130—145) a feeble tertiary maximum can be distinguished, at any

FIG. 1.



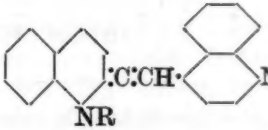
rate in curves IIa and III. In its intermediate position, the 2 : 4′-carbocyanine spectrum thus corresponds with the constitution assigned to the dye, intermediate between those of pinacyanole and kryptocyanine. The chain of conjugated unsaturated linkings by which the two nitrogen atoms in the molecules of these compounds are united contains five atoms in pinacyanole, nine in kryptocyanine, and seven in the new dye.

The spectrum of the new dye is intermediate, not only in position on the scale of wave-numbers, but also in other features. In passing from pinacyanole through this substance to kryptocyanine, the primary band shows a gradual increase in intensity and a diminution in breadth, whilst the intensity of the secondary band shows a similar but more marked decrease, and the tertiary band, which is very distinct in the pinacyanole spectrum, becomes weaker in the new dye and is indistinguishable in kryptocyanine.

It is remarkable that the secondary maxima of kryptocyanine and the 2 : 4′-carbocyanine lie nearly at the same wave-numbers as the primary maxima of the 2 : 4′-carbocyanine and pinacyanole, and that the tertiary maximum of the 2 : 4′-carbocyanine corresponds closely in situation with the secondary maximum of pinacyanole.

Constitution of the Dicyanines.

In undertaking this synthesis of a 2 : 4′-carbocyanine we expected that it would throw light on the constitution of the dicyanines. These are dyes which are formed by the action of an alkali and an oxidising agent (D.R.-P. 155541) on quaternary salts of 2 : 4-dimethylquinoline or its substitution derivatives and are of value as sensitisers for infra-red photography. Detailed descriptions of their preparation have been given by Wise and Adams (*Amer. J. Eng. Chem.*, 1918, **10**, 801) and by Mikeska, Haller, and Adams (*J. Amer. Chem. Soc.*, 1920, **42**, 2392), and their constitution has been discussed by O. Fischer (*J. pr. Chem.*, 1918, [ii], **98**, 209), who suggested for the parent substance of the group the formula VIII or, alternatively, the tautomeric formula with the halogen on the other nitrogen atom.



(VIII.)

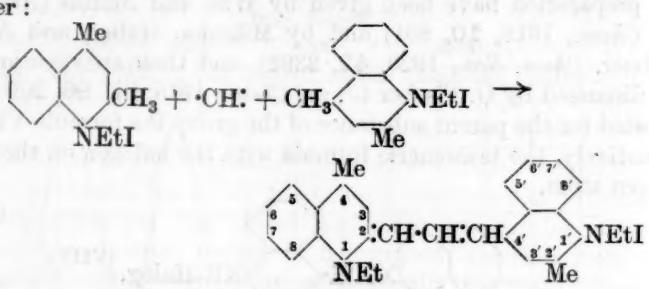
We have investigated the question of the constitution of these dyes in the following manner.

A specimen of dicyanine was prepared from 2 : 4-dimethylquinoline ethiodide and analysed. It was found to have the composition $C_{27}H_{29}N_2I$. The number of carbon atoms in the dye is thus one more than is contained in 2 mols. of dimethylquinoline ethiodide ($C_{13}H_{16}NI$). It must therefore be formed by the condensation of 2 mols. of the ethiodide with a one-carbon residue, the latter proceeding presumably from formaldehyde or some methenyl derivative formed as a by-product in the oxidation in presence of alkali.

It is exceedingly improbable that in a condensation taking place under the conditions in question any part of the molecule of the ethiodides other than the methyl groups could be involved. It may therefore be assumed that in the dicyanine molecule the two quinoline residues are linked by the three-carbon chain :CH·CH:CH·, the two outer methenyl groups of this being derived from the reactive methyl groups of the ethiodide, one from each of the two molecules concerned, the central methenyl group being supplied in the manner referred to above. If this is so, the dicyanine must be the dimethyl

derivative of either pinacyanole, kryptocyanine, or the 2 : 4′-carbocyanine described in this paper, and its spectrum must show a very close relationship to that of one of the three spectra I, IIa, and III in Fig. 1. The extinction coefficients of alcoholic solutions of the dye were therefore measured over a range of wave-lengths in the visible region. They are represented by the dotted line IIb, which is seen to be nearly coincident with the curve IIa representing the absorption spectrum of the 2 : 4′-carbocyanine. When an intimate relationship of this kind is found between the spectra of two dyes only differing in composition by C_2H_4, it must be concluded that they are homologous compounds of the same type.

The dicyanine is accordingly the dimethyl derivative of the 2 : 4′-carbocyanine, its formation taking place in the following manner:



Thus, in this condensation also, the linking is more readily effected between the 2- and the 4′-positions than between the 2- and 2′-, or the 4- and 4′-positions.

The carbocyanine dyes accordingly constitute a well-ordered group of compounds containing three sub-groups corresponding with the three sub-groups of the cyanine dyes proper.

Cyanine Dyes.	*Carbocyanine Dyes.*
2 : 2′-Cyanines; *pseudo*Cyanines.	2 : 2′-Carbocyanines; Pinacyanole, etc.
2 : 4′-Cyanines; *iso*Cyanines.	2 : 4′-Carbocyanines; Dicyanines.
4 : 4′-Cyanines; Cyanines.	4 : 4′-Carbocyanines; Kryptocyanines.

EXPERIMENTAL.

The dried ethonitrates, obtained from lepidine ethiodide (15 grams) and quinaldine ethiodide (15 grams) by treating the aqueous solutions of each with silver nitrate (8·4 grams) and evaporating the filtrates, were dissolved in pyridine (150 c.c.) together with diformylmethylaminodiphenyl disulphide (16·7 grams) (Mills, Clark and Aeschlimann, J., 1923, **123**, 2358) and heated for 7 hours at 100°, when an intense blue colour gradually developed.

The products formed in this operation were (1) the 2 : 4′-carbocyanine, (2) the thio*iso*cyanine, (3) the thio*pseudo*cyanine, (4) pina-

cyanole, (5) kryptocyanine, (6) bis-2-methylbenzothiazoline-1 : 1-spiran (Mills and Braunholtz, *loc. cit.*). All these could be isolated with the exception of kryptocyanine, the presence of which was ascertained spectroscopically.

The thio*iso*cyanine nitrate (A) crystallised from the reaction mixture on standing. To obtain the other products, the filtrate was poured into an aqueous solution of potassium iodide. The tarry material deposited was collected after 3 days, digested with warm water to remove quinaldine and lepidine ethiodides, and then with hot benzene to remove the spiran (B). It was extracted thrice with a mixture of methyl alcohol (5 c.c.) and benzene (15 c.c.), and then dissolved in boiling methyl alcohol, when the nearly pure 2 : 4′-dicyanine was deposited on cooling (filtrate C).

1 : 1′-*Diethyl*-2 : 4′-*carbocyanine Iodide.*—Twice recrystallised from methyl alcohol, the pure dye was obtained (as methyl alcoholate) in needles with a brilliant green lustre, m. p. 240—241° (decomp.) (Found : * C 62·6; H 5·2; I 26·55. $C_{25}H_{25}N_2I$ requires C 62·5; H 5·2; I 26·45 per cent.).

2-*Methyl*-1′-*ethylthio*isocyanine *Iodide.*†—This was obtained by adding the hot alcoholic solution of the crude nitrate (A) to a hot aqueous solution of potassium iodide and crystallising the red, flocculent material, precipitated on cooling, three times from methyl alcohol. Deep red, silky needles, m. p. 248—249°. The constitution of this compound was established by showing its identity with the thio*iso*cyanine obtained in the following manner by the action of pyridine and the disulphide on lepidine ethonitrate.

Lepidine ethonitrate (from lepidine ethiodide, 4·6 grams) and diformylmethylaminodiphenyl disulphide (2·6 grams), dissolved in pyridine (25 c.c.), were heated for 7 hours at 100°. The nitrate which separated on cooling was converted into the iodide as above. The latter, recrystallised from methyl alcohol, was identical in appearance, m. p. and mixed m. p. (248—248·5°) with the iodide from A (Found : C 53·56; H 4·5; N 6·27; S 7·05; I 28·42. $C_{20}H_{19}N_2SI$ requires C 53·8; H 4·26; N 6·28; S 7·17; I 28·40 per cent.).

2-*Methyl*-1′-*ethylthio*pseudo*cyanine Iodide.*—This was contained in the benzene-alcoholic extracts of the crude 2 : 4′-carbocyanine and in the methyl alcoholic filtrate C, and was obtained mixed with much carbocyanine by concentration of these. The purification was effected by making use of the greater ease with which the carbocyanines are converted into soluble colourless diacid salts. Concentrated hydriodic acid was added to the hot alcoholic solution until the blue or green colour had disappeared, leaving a brown solution from which the thio*pseudo*cyanine was precipitated by

* After drying at 110° and 15 mm. † Numbering : J., 1922, **121**, 2005.

addition of water. Crystallised from methyl alcohol, it formed brown, felted needles with a blue lustre, giving a reddish-brown alcoholic solution. M. p. 254—256°. It was identical with the thio*pseudo*cyanine prepared by heating the nitrate from quinaldine ethiodide (9 grams) and diformylmethylaminodiphenyl disulphide (5 grams) with pyridine for 7 hours at 100°. In appearance, the substances were indistinguishable; m. p. and mixed m. p. 254—256° (Found: I 28·14. $C_{20}H_{19}N_2SI$ requires I 28·47 per cent.).

Bis-2-methylbenzothiazoline-1 : 1-spiran.—The benzene extract (B) evaporated left a solid which, crystallised from alcohol and decolorised with animal charcoal, gave the pure spiran, m. p. 207·5—208° (corr.) (Found: C 62·9; H 4·96; N 9·9; S 22·5. Calc., C 62·9; H 4·9; N 9·8; S 22·4 per cent.).

Dicyanine (2' : 4-Dimethyl-1 : 1'-diethyl-2 : 4'-carbocyanine Iodide).—This compound was prepared by Mr. J. A. Aeschlimann by a method based on that described by Mikeska, Haller, and Adams (*loc. cit.*) for the preparation of the dicyanine from 6-ethoxy-2 : 4-dimethylquinoline ethiodide. A solution of 2 : 4-dimethylquinoline ethiodide (9·39 grams) in methyl alcohol (100 c.c.) was cooled until the salt began to separate. A solution of sodium methoxide prepared from sodium (0·345 gram) and methyl alcohol (30 c.c.) was added gradually and the mixture left exposed to the air. It became deep blue and the dicyanine crystallised. It was collected after 36 hours and recrystallised thrice from methyl alcohol. The crystals are olive-green when seen in mass and show a golden lustre. They lose methyl alcohol of crystallisation at 110° and 15 mm. and melt at 244—252° (Found: C 63·98; H 5·59; I 25·19, 25·02. $C_{27}H_{29}N_2I$ requires C 63·8; H 5·71; I 25·0 per cent.).

The Absorption Spectra.

The extinction coefficients ($1/l \cdot \log_{10} I_0/I$) of alcoholic solutions of the dyes were measured with a Nutting spectrophotometer made by Hilger. Solutions rather weaker than millionth-molar were used for the more strongly absorbing regions of the spectrum, stronger solutions for the more weakly absorbing. The extinction coefficients (ϵ) for millionth-molar solutions were calculated from those observed assuming Beer's law to hold, which, over the ranges employed, is very nearly, if not exactly, the case.

The following numbers give the principal points on the curves.

	Primary maxima.		Secondary maxima.		Tertiary maxima.	
	λ.	ε.	λ.	ε.	λ.	ε.
Pinacyanole	6070	0·204	5625	0·088	5192	0·019
2 : 4-Carbocyanine	6570	0·217	6065	0·069	5624	0·015
Dicyanine	6555	0·218	6035	0·063	—	—
Kryptocyanine ...	7115	0·255	6550	0·050	—	—

We desire to express our indebtedness to the Department of Scientific and Industrial Research for a grant to one of us (R. C. O.) by which he was enabled to take part in this work.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE. [*Received, June 28th*, 1924.]

CCXLIII.—*Studies of Valency. Part IV. Absorption Spectra of Camphor, Benzylidenecamphor, and Camphorquinone. Optical Evidence of Two Types of Conjugation.*

By THOMAS MARTIN LOWRY and HELEN SOMERSBY FRENCH.

1. *Methods of Measurement.*—Until recently, measurements of the absorption spectra of organic compounds were generally only qualitative in character. It was therefore not possible to make any direct comparison between the observations of different workers, partly because the results were affected by the form of apparatus and method of working of each observer, but also because different workers interpreted their observations in different ways. The introduction of the sector-photometer reduced very largely this source of uncertainty, by making possible direct measurements of optical density in the ultra-violet, but even these were dependent on the characteristic exposure–density curve of the photographic plate, thus leaving open a real (although probably insignificant) source of error. The recent introduction of an ultra-violet photometer, modelled on the Nutting photometer for visible light, has, however, made it possible to obtain absolute measurements of optical density in the ultra-violet as well as in the visible region, and so to secure when required a direct comparison with absolute measurements in the infra-red. One important result of these newer methods of working is that the existence in organic compounds of an almost universal " general absorption " of light of shorter wave-length than 2300 Å.U. has proved to be largely mythical (compare V. Henri, *Ber.*, 1913, **46**, 3628). This apparent absorption was due mainly to the sudden falling off of intensity of the iron-arc spectrum at 2327 Å.U., a factor which does not affect the accuracy of measurements made by the later quantitative methods, although it makes necessary a longer exposure of the plate. Another factor which helped to produce this apparent general absorption was the growing absorptive power of the solvent. In the older series of measurements, the solvent was generally tested to see that it was reasonably transparent to ultra-violet light of short wave-length; but its

absorptive power was not measured, and no correction was applied for its lack of complete transparency. This effect is, however, now automatically compensated by measuring the optical density of the solution against that of a tube of the solvent. When these obvious sources of error are eliminated, the later measurements often show, as Henri has pointed out, a progressive diminution of absorptive power, where the older qualitative records show a rapid increase of absorption. Many other results, however, flow from the possibility which now exists of making exact numerical comparisons of absorption of light, and one of the most striking of these is discussed below.

2. *Materials and Solvents.*—It has been known since 1906 (Stewart and Baly, J., 1906, **89**, 496) that camphorquinone gives a band in the blue, which appeared to have a greater "persistence" * than in the case of most other organic compounds, including camphor itself. Qualitative measurements showed, however, that the "penetration" * (or maximum density) of the band was very much the same for camphor as for camphorquinone, its lesser persistence being due to its closer contiguity to the region of apparent strong general absorption referred to above (Lowry and Southgate, J., 1910, **97**, 914). The necessity, in connexion with a study of rotatory dispersion, for redetermining the positions of the maxima of absorption in these two compounds gave us the opportunity of comparing more precisely their absorptive power as measured by their "molecular extinction coefficients," † instead of by the "penetration" ‡ of the band. At the same time we took the opportunity of making an exact quantitative comparison of the absorptive power of camphor with that of benzylidenecamphor, which may be regarded as a typical example of the more complex conjugated derivatives.

* The terms "penetration" and "persistence" were used formerly to describe the properties of an absorption band as determined by the qualitative method. The "penetration" can, however, now be expressed quantitatively by the function log ϵ (max.), as defined below, whilst its "persistence" is given by the function log ϵ (max.) − log ϵ (min.).

† This is expressed (following V. Henri, *Ber.*, 1912, **45**, 2820) by the relation $I = I_0 . 10^{-\epsilon c d}$, where ϵ = the molecular extinction coefficient, c = the molecular concentration of the solution in gram-mols. per litre, and d = the thickness, in centimetres, of the layer of solution.

‡ The "penetrations" recorded in my earlier papers (J., 1909, **95**, 807, 1340; 1910, **97**, 899, 905) in the form of "log. thickness in millimetres of millinormal solution" can be converted in a rough general manner into "molecular extinction coefficients" by subtracting this logarithm from an instrumental constant (the value of which is about 4·4) and thus obtaining an approximate value for log ϵ. The corresponding constant for Baly's instrument appears to have been very similar (4·0 to 4·5), although his data were usually plotted on a different scale.—T.M.L.

Absorption curves obtained by the qualitative method have already been given, for solutions in *alcohol*, (i) of camphor by Hartley, Baly, Henderson, Purvis, and Lowry (see *Rep. Brit. Assoc.*, 1916, p. 141), (ii) of camphorquinone by Stewart and Baly (*loc. cit.*), and (iii) of benzylidenecamphor by Lowry and Southgate (J., 1910, **97**, 905). The quantitative observations now recorded include measurements of the molecular extinction coefficients of all three compounds in alcoholic solutions; but solutions of camphor in *cyclo*hexane and in benzene, and of camphorquinone in benzene were also examined, both in the form of long columns (1 to 10 cm.) of a dilute solution, and of thin films of much higher concentration, with a view to securing absorption data which could be compared directly with observations of rotatory dispersion in solutions of similar strength.

3. *Experimental Results.*—(*a*) The position of the *head of the band* for each of these solutions is shown in the following table.

Solute.	Solvent.	Concentration.	Log ϵ.	λ.
Camphorquinone.	Alcohol.	*M*/250	1·46	4650
,,	Benzene.	*M*/250	1·55	4650
,,	,,	15 g./100 c.c.	—	4700
Camphor.	Alcohol.	*M*/100	1·57	2880
,,	*cyclo*Hexane.	*M*/100	1·45	2880
,,	,,	20 g./100 c.c.	—	2900
,,	Benzene.	7 g./100 c.c.	1·57 (?)	2880
Benzylidenecamphor.	Alcohol.	*M*/40,000	4·32	2900

These numerical results are very striking. The position of the band, both in camphor and in camphorquinone, is remarkably steady, and is almost independent of the solvent and concentration. On passing from camphor to camphorquinone, however, the band at 2880 Å.U. is shifted through some 1800 Å.U. to 4650 Å.U.; but this shift is not accompanied by any appreciable change of intensity, since log ϵ remains unaltered at 1·5. *The development of visible colour is therefore not accompanied by any increase in the absorptive power of the compound,** but only by a displacement of the band from the ultra-violet to the visible region. On the other hand, on comparing a solution of camphor in alcohol with a solution of benzylidenecamphor in the same solvent, the maximum value of the molecular extinction-coefficient is increased more than 500-fold, from log $\epsilon = 1{\cdot}57$ to 4·32, ratio 1 to 563, but *the wave-length of*

* A comparison of the earlier curves for camphor and camphorquinone, as recorded by two different observers, suggested that the molecular absorptive power of camphorquinone was *greater* than that of camphor in the ratio 1·7 to 1, corresponding roughly with the presence of *two* carbonyl groups instead of *one*. This ratio is now shown not to differ substantially from unity.

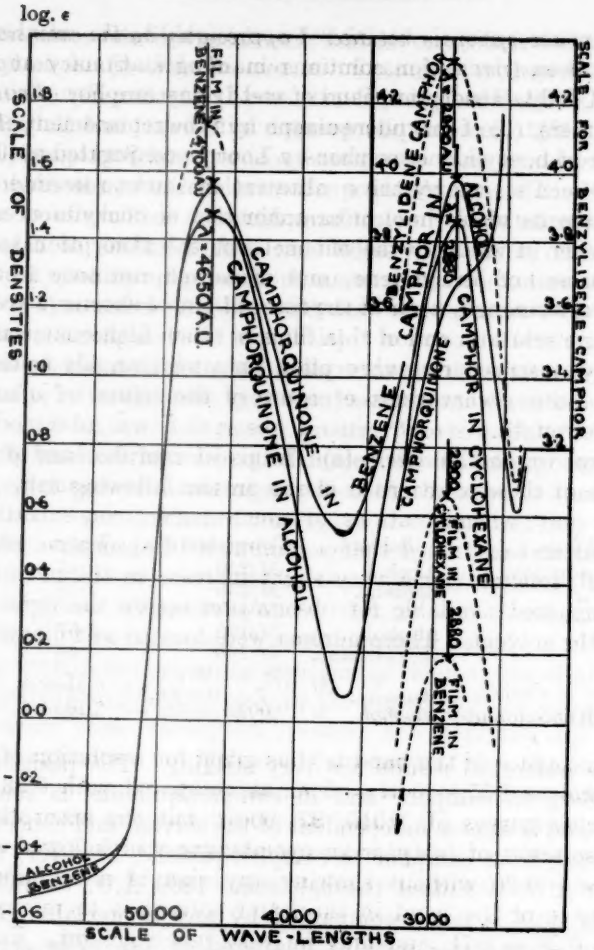


FIG. 1.—*Absorption Spectra of Camphor, Camphorquinone, and Benzylidene-camphor.*

A different scale of densities has been used for the dotted curves. The scale for benzylidenecamphor is shown on the right hand of the diagram. The scales of densities for the thin films of concentrated solutions are arbitrary, since the thickness of the films was not known, and only relative densities could be given.

The ultra-violet absorption spectrum of camphorquinone is shown for an alcoholic solution of concentration $M/75$. It is not continuous with the spectrum for a concentration of $M/10$, which it approaches (but does not meet) at a wave-length of about 3250 Å.U. The curve for $M/10$ concentration is, however, continuous with the curve for $M/75$ in the neighbourhood of the visible band. Identical readings were also obtained for the head of the band by the visual method at a concentration of $M/250$ and by the photographic method at a concentration of $M/75$. Beer's law appears therefore to hold good in the visible spectrum but not in the ultra-violet region.

maximum absorption is not altered appreciably by the extension of the conjugated system, the maximum remaining stationary at 2880 to 2900 Å.U. The absorption band of methylenecamphor (a compound which differs from benzylidenecamphor in the replacement of phenyl by hydrogen, so that it contains a shorter conjugated system) has already been shown by the qualitative method to be intermediate in position between those of camphor and of benzylidenecamphor.

(*b*) When studied by the old method, the absorption spectra of camphor and of benzylidenecamphor showed, not only a band, but also a very strong *general absorption* of light of shorter wave-length. This "general absorption" (although often fictitious) was indeed formerly observed on every plate on which an absorption band could be seen, whatever the nature of the solute. No indication whatever of this strong general absorption was obtained on the plates on which the absorption bands of camphor and of benzylidenecamphor were recorded in the present investigation. Indeed, it was only when solutions of much higher concentration were prepared and examined that a minimum of absorptive power was detected, followed by a very slight increase in the narrow region that remained available for observation before the light was cut off by the solvent. These minima were located as follows:

Camphor in alcohol.	$M/10$.	$\log \epsilon = 0{\cdot}61$ at $\lambda = 2400$.
Benzylidenecamphor in alcohol.	$M/10{,}000$.	$\log \epsilon = 3{\cdot}10$ at $\lambda = 2400$.

The persistence of the band is thus given for a solution of *camphor in alcohol* as $1{\cdot}57 - 0{\cdot}61 = 0{\cdot}96$, as compared with 0·28 only on the earlier curves (J., 1910, **97**, 906); but the absorption of an $M/10$ solution of *camphor in* cyclo*hexane* was followed as far as $\log \epsilon = -0{\cdot}26$ without showing any sign of a minimum. The persistence of the band in the latter solvent is therefore at least $1{\cdot}45 + 0{\cdot}26 = 1{\cdot}71$, and may be very much greater. For *benzylidenecamphor in alcohol* the persistence of the band is now given as $4{\cdot}32 - 3{\cdot}10 = 1{\cdot}22$, as compared with the earlier value of 0·67. The minima for camphorquinone were located as follows:

In alcohol.	$M/10$.	$\log \epsilon = 0{\cdot}08$ at 3650 Å.U.;	persistence 1·38.
In benzene.	$M/250$.	$\log \epsilon = 0{\cdot}58$ at 3700 Å.U.;	,, 0·97.

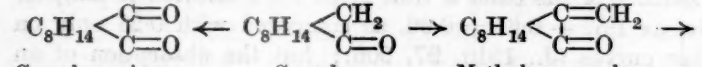
The persistence, 1·38, of the band in alcohol is substantially less than the value 1·8 recorded by Baly for a more dilute solution, whilst the persistence, 0·97, of the band in benzene is still smaller and agrees closely with the persistence of the camphor band in alcohol. The relatively low persistence previously recorded for the band of camphor and of benzylidenecamphor is thus seen to have been due to a gross over-estimation of the general absorption

in these compounds. It may be noted, however, that the range of wave-length from the maximum to the minimum is twice as great in camphorquinone, where it amounts to 4650 — 3650 = 1000 Å.U., as it is in camphor and in benzylidenecamphor, where it amounts only to 2900 — 2400 = 500 Å.U.

(*c*) In the case of camphorquinone, in addition to a general absorption (rising to the level of the head of the band at a wave-length of about 2600 Å.U.), a marked *step-out*, which has not been detected previously, was seen at log $\epsilon = 1{\cdot}3$, $\lambda = 2850$ approximately, in very fair agreement with the position of the original camphor band. This step-out was at first recorded only as a discontinuity on two consecutive photographic plates, but was shown quite unmistakably on a subsequent plate, which covered the range of densities from log $\epsilon = 0{\cdot}6$ to $1{\cdot}7$, and on which the horizontal "step-out" extended over about an inch.

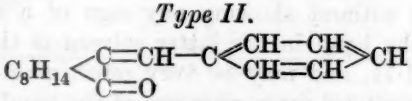
4. *Conclusions.*—In considering these results, it is evident that the characteristic ketonic band of camphor can be displaced in two ways, by altering *either* the wave-length of the maximum absorption *or* its intensity, whilst leaving the other constant of the band unchanged. The one change is effected by introducing a second carbonyl group in a position which Thiele would have regarded as conjugated; the other change is also produced by extending the conjugated chain; thus

Type I. *Type II.*



Camphorquinone. Camphor. Methylenecamphor.

Type II.



Benzylidenecamphor.

The two types of conjugation differ in that one contains two opposing "key atoms," thus giving rise to an obvious case of "crossed polarities," whilst the second contains only one of these "key-atoms," so that the polarities will naturally be concordant. Precisely the same conditions prevail in the quinones of the aromatic series, including not only the *o*-quinones, but also the *p*-quinones, although the two opposing carbonyl groups in the latter are separated by ethylenic linkings instead of being contiguous. The fact that these quinones show a band in almost exactly the same position as that of camphorquinone (Baly and Stewart, J., 1906, **89**, 502) suggests that the displacement of the ketonic band from the ultra-

violet into the visible region may be attributed to similar causes in the two types of diketone. It is, however, not suggested that the development of visible colour in organic compounds is invariably due to crossed polarities, nor even that crossed polarities necessarily have a "bathochromic" influence (compare Kundt, *Pogg. Ann.*, 1874, Jübel-band, 615). The experimental data now recorded establish with peculiar sharpness, however, the fact that the development of a long conjugated chain is not in itself sufficient to produce visible colour, since in the cases under consideration the passive ethylenic groups serve merely to enhance the efficiency of the more active carbonyl group, to which the selective absorption in the ultra-violet is primarily due, but without altering its natural frequency. Some second factor, in addition to an extended alternation of single and double bonds, is therefore needed to bring the natural frequency of the system down to the limits of visibility. In the quinones, this factor seems to be supplied by the presence of two doubly-bound oxygen atoms at the ends of a conjugated chain; but there are obviously many other ways in which the same effect may be produced.

Summary.

A solution of camphor in alcohol shows a band at $\log \epsilon = 1{\cdot}57$, $\lambda = 2880$ Å.U. In benzylidenecamphor the band is moved to $\log \epsilon = 4{\cdot}32$, but the wave-length is practically constant at 2900 Å.U. In camphorquinone the wave-length is altered to 4650 Å.U., but the intensity remains practically constant at $\log \epsilon = 1{\cdot}46$. These observations are used as evidence of the existence of two different types of conjugation (compare J., 1923, **123**, 825); their bearing on the origin of visible colour is also discussed.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

[*Received, June 4th*, 1924.]

CCXLIV.—*The Chemistry of the Glutaconic Acids. Part XVI. Three-carbon Tautomerism in the* cyclo-*Propane Series. Part III. Refractometric Evidence.*

By FRANK ROBERT GOSS, CHRISTOPHER KELK INGOLD, and JOCELYN FIELD THORPE.

IT is now well known (compare Drude, "Theory of Optics"; Kayser, "Handbuch der Spektroscopie," Bd. 4; Richardson, "The Electron Theory of Matter"; Pickard and Hunter, J., 1923, **123**, 434; Hunter, *ibid.*, p. 1671) that the so-called exaltation of re-

fractivity, which was at one time regarded as an almost infallible criterion in structural problems, is, in reality, only a manifestation of the existence of one or more absorption bands at no great distance from that portion of the spectrum at which the measurement of refractive index is made. Since experimental convenience in obtaining a monochromatic beam alone governs the choice of a wave-length for measurement, and since any fixed wave-length will be differently related to the main features of the absorption spectra of different substances, the exaltations of "spectro-chemistry" are seen to be devoid of any direct physical or philosophical significance. It is therefore not surprising that the elementary spectro-chemical "constants" are by no means constant, that the exaltations ascribed to any given molecular feature may vary from nothing to a large value, and that in order to obtain even superficial agreement from figures relating to substances of known structure comparisons frequently have to be restricted to compounds which, arguing back from the results, can safely be pronounced to be of the same "optical family." The weakness of these methods in the solution of modern structural problems is made evident by many well-known examples, amongst which the cases of benzene, furan, and the intra-annular tautomeric compounds prepared in these laboratories (compare Toironen, *Soc. Sci. Fennica Comm. Phys.-Math.*, 1923, **1**, Nr. 26) may be cited. In the solution of such problems structural organic chemistry has, in our opinion, little to gain at present from refractivity determinations; nor can it have until the whole field offered by organic structures no longer in debate has been explored with the aid of an adequately founded dispersion formula, a task not yet begun.

It is surprising to note that Auwers and Ottens continue to regard spectro-chemical calculations as constituting serious evidence in structural problems of this class. In a recent paper (*Ber.*, 1924, **57**, 437) they record the refractivities of three glutaconic esters,* the β-methyl, αβ-dimethyl, and β-methyl-α-ethyl derivatives, each in its two isomeric modifications. Exaltations were obtained of similar orders of magnitude for each pair of isomerides, but differing in the several cases by some hundreds per cent.; and on the basis of these results alone, without reference to the chemical evidence, or to the crucial test cases under examination in these laboratories, the conclusion was drawn that the isomerism of the glutaconic esters is geometrical in character. When it is reflected that the mobile

* Similar determinations had been made, with practically identical results, by Dr. G. A. R. Kon in this laboratory, before the publication of Auwers and Ottens's paper; and his view as to the structural significance of the results is in entire agreement with that expressed in this paper.

three-carbon system represents ground unexplored even by the customary empirical methods of spectro-chemistry, and that the esters which Auwers and Ottens (following Feist) designate as "*trans*," should by a strict spectro-chemical interpretation of their results be "*cis*," * it becomes difficult to understand how these investigators have been drawn to such a conclusion against all the chemical evidence.

If any further proof were required of the weakness of spectro-chemical methods in structural problems such as that under discussion, it is to be found in the measurements which we have recently made of the refractive indices of those glutaconic esters *in which geometrical isomerism is excluded by ring formation* (Goss, Ingold, and Thorpe, J., 1923, **123**, 327, 3342). Results closely comparable with those of Auwers and Ottens have been obtained. Both the normal and labile isomerides show marked exaltations, similar in relative value and order of magnitude to those displayed by the various pairs of isomeric open-chain glutaconic esters which Auwers and Ottens have examined. The data are set forth in the following tables, in the second of which some figures relating to αβ-dimethylglutaconic ester are included for comparison. A noteworthy feature, extraordinary from the customary spectro-chemical view of geometrical isomerides, but shown both by our own and by Auwers and Ottens's results, is that the normal compound (that belonging to the series which Feist terms "*trans*") has the smaller refractivity.

Refractivities of Isomeric Forms of Ethyl 2-Methyl-Δ¹-cyclopropenedicarboxylate.

Modification.	M.	t.	$d_4^{t°}$.	$n_D^{t°}$.	$[R_L]_D = \frac{n^2_D - 1}{n^2_D + 2} \cdot \frac{M}{d}$.	$[R_L]_D$ (mean).
Normal.	198·11	18·7°	1·0661	1·4586	50·77	*50·71*
		18·7	1·0661	1·4584	50·66	
Labile.	198·11	18·9	1·0715	1·4633	50·95	*50·94*
		19·4	1·0715	1·4628	50·94	

Exaltations of Isomeric Ring Glutaconic Esters and of Isomeric Open-chain Glutaconic Esters.

Ethyl ester.	Modification.	$[R_L]_D$ (obs).	$[R_L]_D$ (calc).	Exaltations.	Observers.
Methyl-ring-ester.	Normal.	50·71	49·72*	*0·99*	Goss, Ingold, and Thorpe.
	Labile.	50·94	49·72*	*1·22*	
Dimethylglutaconic ester.	Normal.	56·42	55·84	*0·58*	Auwers and Ottens.
	Labile.	56·57	55·84	*0·73*	

* Allowing 0·7 for *cyclo*propane ring formation.

* The observed differences being in this sense (cf. table).

How Auwers and Ottens would extend their geometrical theory to cover the case of the cyclic esters we do not know; but unless an adequate explanation can be given of the reproduction in the cyclic series of the characteristic features of glutaconic isomerism the conclusions of these investigators must remain discredited.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, April 29th*, 1924.]

CCXLV.—*Fission of the Pyridine Nucleus During Reduction.*

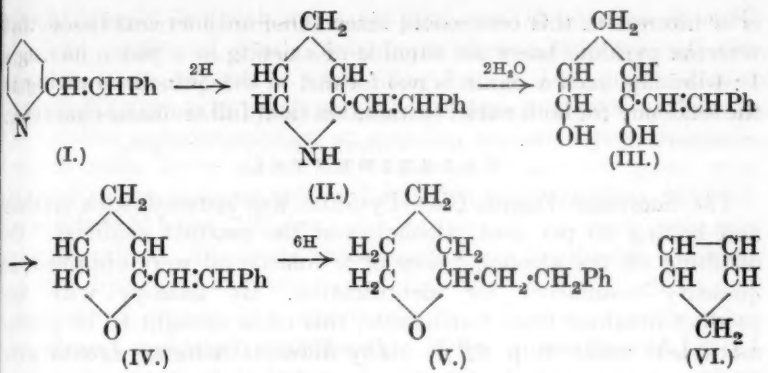
By BRIAN DUNCAN SHAW.

ALTHOUGH it is known that the pyridinecarboxylic acids can be converted into nitrogen-free compounds by reduction with sodium amalgam and water (Mumm and Brodersen, *Ber.*, 1923, **56**, [*B*], 2295), the fact that pyridine itself is capable of undergoing a similar change seems to be unrecorded.

If 95 per cent. alcohol is substituted for absolute alcohol in the preparation of piperidine by Ladenburg's method, little or none of this base is produced, ammonia is evolved, and the main product is a brown, non-nitrogenous resin; a trace of a colourless, volatile, saturated oil is also formed. Only a small proportion of the pyridine can be recovered.

Quantitative experiments were made in which pyridine was reduced by a definite weight of sodium of known hydrogen value. By measuring the volume of hydrogen unabsorbed and estimating the amount of ammonia produced, it was found that the ring fission occurs at the dihydro-stage of the reduction. The resin formed is not further reducible, so that, when water is present, 1 mol. of pyridine should require only 1 mol. of hydrogen for its conversion into the resin and ammonia. In practice, rather more than this quantity is absorbed, since small amounts of piperidine and of the saturated volatile oil are formed.

Other bases containing a pyridine nucleus were subjected to reduction with sodium and aqueous alcohol. The picolines, 2 : 6-lutidine, 2-methyl-5-ethylpyridine, 1-ethylpyridone, and 2-aminopyridine all gave ammonia, but the most definite results were obtained with 2-stilbazole (I). The main product from this base is 2-β-*phenylethyltetrahydropyran* (V), the formation of which, coupled with the quantitative evidence already cited, indicates that the course of the reaction is as follows:



The production of ammonia from pyridine itself is the result of the hydrolysis of a dihydropyridine corresponding to the 1 : 4-dihydrostilbazole (II). Now the ·CH:CH· groups in *cyclo*pentadiene (VI), functioning like carbonyl groups, render the hydrogen of the methylene group displaceable by metals. 1 : 4-Dihydrostilbazole is analogously constituted and therefore should display the properties of an acid imide, and be hydrolysable to the diol (III); loss of water and further reduction would give the pyran (V). The 1 : 4-dihydro-structure ascribed to (II) is based partly on the theoretical reasoning already given, but mainly on the fact that the only dihydropyridine derivatives which are known to be hydrolysable with production of ammonia are 1 : 4-dihydro-compounds (compare Cohnheim, *Ber.*, 1898, **31**, 1033; Knoevenagel and Ruschaupt, *Ber.*, 1898, **31**, 1025). The production of so much resin from pyridine is readily explicable, since the glutardialdehyde corresponding to III would be rapidly attacked by alkali.

The above scheme is supported by the work of Mumm and Brodersen (*loc. cit.*), which was published while the present investigation was in progress.

The pyridine ring in 2-stilbazole is more readily reduced by sodium and alcohol than the ethylene linking in the side chain, for 90 per cent. of the basic matter remaining in the reaction mixture after reduction is unchanged stilbazole.

All the compounds of the pyridine series to which the reaction has been applied gave ammonia quite readily. On the other hand, the most drastic treatment failed to produce a like effect with either quinoline or *iso*quinoline. This difference in behaviour can scarcely be due to the steric influence of the benzene nucleus. A probable explanation is that in the case of the quinolines the first product of reduction is a stable 1 : 2-dihydro-derivative instead of a hydrolysable 1 : 4-compound. The work of Mills and Smith (J., 1922, **121**, 2724)

is of interest in this connexion, since these authors concluded that whereas pyridine bases are capable of existing in a phase having a 1 : 4-linking, such a phase is not formed in the quinolines owing to the tendency for both nuclei to maintain their full aromatic character.

EXPERIMENTAL.

The Saturated Volatile Oil.—Pyridine was reduced with sodium and boiling 95 per cent. alcohol, and the product acidified. On distilling off the alcohol, traces of a volatile oil were obtained, in quantity insufficient for identification. By analogy with the product obtained from 2-stilbazole, this oil is thought to be pentamethylene oxide (b. p. 82°). Many different reducing agents were tried in the hope of obtaining more of the oil, but without success. The experiments showed, however, that ring fission occurred only when water was present and the solution was allowed to become hot.

Quantitative Experiments.—Pyridine (10 gms.) was reduced with sodium (16·5 gms.; hydrogen value 7,311 c.c.) and boiling 95 per cent. alcohol (250 c.c.). The ammonia produced was separated from pyridine and estimated by Prideaux's method (*Trans. Faraday Soc.*, 1919, **15**, 137). It was thus found that 7·7 gms. of pyridine had been decomposed. The hydrogen evolved during the reduction measured 4,250 c.c. (corr.). Therefore 7·7 gms. of pyridine had taken up 3061 c.c. of hydrogen before decomposition (Calc. for dihydropyridine 2,183 c.c.; for tetrahydropyridine 4,366 c.c.).

2-*Stilbazole* was prepared by a modification of Baurath's method (*Ber.*, 1887, **20**, 2719; 1888, **21**, 818), a large excess of benzaldehyde being used to convert any 2 : 6-lutidine present into 2 : 6-distyrylpyridine. α-Picoline (16 gms.) was heated with benzaldehyde (24 gms.) and zinc chloride (5 gms.) in a sealed tube for 8 hours at 220°. The product was colourless or yellow to dark brown, according as pure picoline or base containing lutidine was used. The zinc chloride and excess of benzaldehyde were removed, the base was dissolved in dilute hydrochloric acid, the solution filtered from 2 : 6-distyrylpyridine hydrochloride, and the stilbazole precipitated from the filtrate, and recrystallised from alcohol.

2-Stilbazole was also prepared in quantity from the mixture of pyridine bases boiling from 120—135°, an autoclave being used. The fraction of the crude basic product, b. p. 195—205°/15 mm., was nearly pure stilbazole; the residue was a mixture of stilbazole, methyl stilbazole, and 2 : 6-distyrylpyridine.

Reduction of 2-Stilbazole with Sodium and Aqueous Alcohol.—The base (100 gms.) was reduced with sodium (110 gms.) and boiling 95 per cent. alcohol (1500 c.c.), ammonia being evolved freely. The

product was diluted with water, acidified, and the alcohol distilled off. The brown oil which had separated was removed and the aqueous layer extracted with chloroform. The crude fission product (89 gms. after removal of chloroform) contained stilbazole. The residual aqueous solution on standing deposited pure stilbazole hydrochloride, from which the unchanged base (10 gms.) was obtained. The aqueous mother-liquor, on neutralisation, gave an oily mixture of bases (1·5 gms.) which appeared to contain stilbazole and stilbazoline. The crude fission product was dissolved in benzene, and dry hydrogen chloride passed into the solution. Stilbazole hydrochloride was at first precipitated, but redissolved as the solution became saturated with the gas; it was reprecipitated by removing the excess of hydrogen chloride on the water-bath. After filtration, the benzene was removed. About 10 per cent. of the residue distilled at 190—210°/15 mm., and one-third of the remainder at 210—280°/15 mm. The more volatile portion was fractionally precipitated with light petroleum from benzene solution and a very small amount of a crystalline compound was thus obtained. As this substance was saturated whereas the oily residue was unsaturated, the whole of the original fission product was repeatedly reduced with sodium and amyl alcohol. Thereafter the product gave a large fraction, b. p. 185—195°/15 mm., which solidified when cooled. Recrystallised from benzene and again from light petroleum, the substance formed lustrous plates, m. p. 77°, very easily soluble in most organic solvents, sparingly soluble in light petroleum [Found: C = 82·2; H = 9·6; M (in freezing benzene) = 193. $C_{13}H_{18}O$ requires C = 82·1; H = 9·5 per cent.; M = 190]. The molecular formula and chemical properties leave little doubt that the compound is 2-β-*phenylethyltetrahydropyran* (V). Dihalogen derivatives of phenylheptane were formed from it by treatment with halogen hydrides, but could not be obtained pure. Hydrogen iodide yielded an unstable viscous *di-iodo*-compound, and hydrogen bromide an oily *dibromide* which readily lost hydrogen bromide, a substance, which appeared to be a mixture of unsaturated bromo-compounds, being produced.

Summary.

Pyridine bases undergo ring fission when reduced with sodium in hot aqueous alcohol. The fission is due to the hydrolysis of an intermediate dihydro-derivative. The final product from 2-stilbazole is 2-β-phenylethyltetrahydropyran.

The author is indebted to Professor F. S. Kipping, F.R.S., for his interest in this work, and to the Department of Scientific and

Industrial Research for a maintenance grant. He also wishes to thank the South Metropolitan Gas Company for gifts of pyridine and α-picoline.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, June 3rd,* 1924.]

CCXLVI.—*Studies in the Phenylsuccinic Acid Series. Part VIII. The Resolution of* r-*Diphenylsuccinalic and* r-*Diphenylsuccino*-p-*toluidic Acids into their Optical Antipodes.*

By HENRY WREN and RICHARD ELLIS BURROWS.

THE resolution of *r*-diphenylsuccinalic and *r*-diphenylsuccino-*p*-toluidic acids (Wren and Williams, J., 1918, **113**, 838) has now been effected by the alkaloidal method. The active acids exhibit the characteristically high specific rotation of the active diphenylsuccinic acids and their simple derivatives. They are readily transformed into the corresponding active anils and *p*-tolils. The specific rotations of these compounds are much lower than those of the acids from which they are derived. This is also the case with the active diphenylsuccinic anhydrides (Wren and Still, J., 1915, **107**, 1457), and exceptions to the rule that the conversion of an acyclic into a cyclic compound is accompanied by enhanced specific rotation (Cohen, " Organic Chemistry," 1920, Vol. II, p. 225) seem thus to have been found. The production of optically active anils and *p*-tolils establishes the relationship of the parent acids to *r*-diphenylsuccinic acid, thus confirming the conclusion drawn by Wren and Williams (*loc. cit.*) from a study of the properties of the acids themselves. The alternative possibility that configurational change occurs during the opening of the diphenylsuccinic anhydride ring (as is observed to some extent under the influence of water or an alcohol) is excluded, since the cyclic compound derived from an active acid related to the *meso*-series must of necessity be optically inactive owing to the restored similarity of the grouping around the two asymmetric carbon atoms and consequent internal compensation. The ease of racemisation of the active anils and *p*-tolils under the influence of a trace of alkali is remarkable and greatly exceeds that of the esters of the active diphenylsuccinic acids, so that the tendency towards enolisation, $\begin{matrix}\text{CHPh·CO}\\|\\\text{CHPh·CO}\end{matrix}\!\!>\!\text{NAr} \rightleftharpoons \begin{matrix}\text{CHPh—CO}\\|\\\text{CPh:C(OH)}\end{matrix}\!\!>\!\text{NAr}$, appears to be much greater in the cyclic than in the acyclic forms.

During the isolation of *d*-diphenylsuccino-*p*-toluidic acid by crystallisation of a mixture of the *r*- and *d*-acids from ethyl alcohol it was observed that the acid remaining in the mother-liquors contained, under certain conditions, an excess of the lævo-isomeride. A similar observation was recorded in the case of the diphenylsuccinic acids (Wren and Still, J., 1915, **107**, 451). It is the experience of one of us (H. W.) that the incidence of the phenomenon is very uncertain and, apparently, dependent on uncontrollable factors.

Experimental.

Resolution of r-*Diphenylsuccinalic Acid into its Optical Antipodes.*—A solution of *r*-diphenylsuccinalic acid (40 gms.) and quinine (40 gms.) in boiling rectified spirit (1000 c.c.) was allowed to cool to the atmospheric temperature, and the needles (46·7 gms.) that slowly separated were crystallised four times from the same solvent. The non-homogeneous quinine *l*-diphenylsuccinalate (15·9 gms.) obtained was decomposed with dilute sulphuric acid and ether, and the l-*diphenylsuccinalic acid* (8·1 gms.; $[\alpha]_D$ − 326·6° in acetone) crystallised from rectified spirit until the specific rotation remained constant. It melted and evolved gas at 193—194° after shrinkage at 187°, then re-solidified, and again melted at 224—226°; the observed values depend somewhat on the mode of heating (Found: C = 76·7; H = 5·6; N = 4·3. $C_{22}H_{19}O_3N$ requires C = 76·5; H = 5·6; N = 4·1 per cent.). In acetone: $l = 2$, $c = 1{\cdot}226$, $\alpha_D^{10\cdot2°}$ − 8·29°, whence $[\alpha]_D^{10\cdot2°}$ − 338·2°; in ethyl alcohol: $l = 2$, $c = 1{\cdot}2384$, $\alpha_D^{15°}$ − 8·68°, whence $[\alpha]_D^{15°}$ − 350·3°.

d-Diphenylsuccinalic acid ($[\alpha]_D$ + 143·6° in acetone, 17·2 gms.; from the crude, dextrorotatory mixture of acids obtained from the first filtrates of the quinine salt) and cinchonine (14·9 gms.) were dissolved in boiling ethyl alcohol (250 c.c.), the cool solution was filtered from a small amount of diphenylsuccinanil, the formation of which is somewhat liable to complicate the course of the resolution, and the filtrate allowed to evaporate spontaneously to about 180 c.c. The non-homogeneous cinchonine *d*-diphenylsuccinalate (19·2 gms.) that separated was decomposed in the usual manner, and the d-*diphenylsuccinalic acid* ($[\alpha]_D$ + 257·7° in acetone) repeatedly crystallised from rectified spirit. The pure acid resembled exactly its optical antipode in appearance, solubility, and melting point. It had $[\alpha]_D^{13°}$ + 337·8° in acetone solution ($l = 2$, $c = 1{\cdot}236$, $\alpha_D^{13°}$ + 8·35°) (Found: C = 76·8; H = 5·7; N = 4·3 per cent.).

l-*Diphenylsuccinanil*, minute prisms, from ethyl alcohol, m. p. 196—196·5° after slight previous softening, was prepared by the action of boiling ethyl alcoholic hydrogen chloride (3 per cent.) on the acid (Found: C = 80·5; H = 5·2; N = 4·6. $C_{22}H_{17}O_2N$

requires C = 80·7; H = 5·2; N = 4·3 per cent.). In chloroform solution: $l = 2$, $c = 1·2248$, $\alpha_D^{13·6°} - 2·88°$; $[\alpha]_D^{13·6°} - 117·6°$.

Dehydration of *l*-diphenylsuccinalic acid is also effected by acetyl chloride at 40°, but the change appears to be accompanied by slight racemisation, since the anil, crystallised once from alcohol, has $[\alpha]_D^{15°} - 111·5°$ in chloroform.

Heated at 195° until evolution of gas ceased, *l*-diphenylsuccinalic acid was converted quantitatively into *r*-diphenylsuccinanil, m. p. 230° (see Wren and Williams, *loc. cit.*).

d-*Diphenylsuccinanil*, m. p. 196—196·5° after slight previous softening, resembles exactly the *l*-isomeride (Found: C = 80·8; H = 5·4; N = 4·5 per cent.). In chloroform: $l = 2$, $c = 1·2608$, $\alpha_D^{17°} + 3·05°$, whence $[\alpha]_D^{17°} + 121·0°$.

Resolution of r-*Diphenylsuccino*-p-*toluidic Acid into its Optical Antipodes.*—Hot solutions of *r*-diphenylsuccino-*p*-toluidic acid (38·0 gms.) and of quinine (19·8 gms.) in ethyl alcohol (950 c.c.) were mixed, and crystals (29 gms.) separated readily. The solid was repeatedly extracted with boiling ethyl alcohol in portions of 500 c.c., the solutions being cooled to the atmospheric temperature previous to filtration. The specific rotations in acetone of the acids isolated from the successive filtrates were + 144·8°, + 279·4°, + 134·5°, + 49·2°, − 2·92°, − 91·62°, − 160·7°, and − 235·7°. The residual quinine salt (18·75 gms.) was decomposed with sulphuric acid and much ether, and the l-*diphenylsuccino*-p-*toluidic acid* (9·65 gms.; $[\alpha]_D^{12·8°} - 327·6°$ in acetone) crystallised from alcohol until the specific rotation was constant: small needles, m. p. 209—209·5° (the observed m. p. depends very greatly on the experimental conditions) (Found: C = 76·7; H = 6·1; N = 4·0. $C_{23}H_{21}O_3N$ requires C = 76·8; H = 5·9; N = 3·9 per cent.). In acetone: $l = 2$, $c = 1·460$, $\alpha_D^{18·8°} - 9·62°$, whence $[\alpha]_D^{18·8°} - 329·5°$.

The isolation of *d*-diphenylsuccino-*p*-toluidic acid was effected by the crystallisation of a mixture of the *d*- and *r*-acids, having $[\alpha]_D + 144·8°$ in acetone, from aqueous ethyl alcohol. After a single crystallisation, the acid had $[\alpha]_D + 202·7°$ in acetone, and the filtrate was decidedly lævorotatory. Repeated crystallisation of the acid from alcohol yielded d-*diphenylsuccino*-p-*toluidic acid*, minute needles, which resembles exactly its optical antipode (Found: C = 76·9; H = 5·9; N = 4·0 per cent.). In acetone: $l = 2$, $c = 1·2028$, $\alpha_D^{16°} + 7·94°$, whence $[\alpha]_D^{16°} + 330·0°$.

d-*Diphenylsuccino*-p-*tolil*, prepared similarly to the active anils, separates from ethyl alcohol in long, colourless needles which not infrequently crumble to microscopic prisms when preserved beneath the mother-liquor. In this respect it resembles the corresponding racemic compound (Wren and Williams, *loc. cit.*). It melts at 178°

after slight softening at 176° (Found: C = 80·8; H = 5·8. $C_{23}H_{19}O_2N$ requires C = 80·9; H = 5·6 per cent.). In acetone: $l = 2$, $c = 1·0544$, $\alpha_D^{15°} + 2·77°$, whence $[\alpha]_D^{15°} + 131·3°$.

d-Diphenylsuccino-*p*-tolil does not appear to undergo autoracemisation when preserved at the atmospheric temperature, when heated at 100° during 2 hours, or when its alcoholic solution is boiled. It is, however, extremely sensitive to the action of alkali; a saturated solution in ethyl alcohol ($\alpha_D + 0·36°$ in a 2-dcm. tube) was treated with 0·5 c.c. of a dilute alcoholic sodium ethoxide, whereby complete racemisation was induced before a further polarimetric measurement could be taken.

l-*Diphenylsuccino*-p-*tolil* resembles exactly its optical antipode in crystalline form, solubility, and melting point (Found: C = 81·1; H = 5·7 per cent.). In acetone: $l = 2$, $c = 1·0996$, $\alpha_D^{16·4°} - 2·89°$, whence $[\alpha]_D^{16·4°} - 131·5°$; in chloroform: $l = 2$, $c = 1·2068$, $\alpha_D^{16°} - 3·29°$, whence $[\alpha]_D^{16°} - 136·3°$.

The authors desire to express their gratitude to the Research Fund Committee of the Royal Society for a grant which has defrayed a part of the expense of this investigation.

MUNICIPAL COLLEGE OF TECHNOLOGY,
BELFAST.

[*Received, May 21st*, 1924.]

CCXLVII.—*The Volumetric Estimation of Total Carbonic Acid in Dilute Solutions of Calcium Hydrogen Carbonate or in Hard Tap-waters.*

By EDWARD MORTIMER CROWTHER and WALLACE STANLEY MARTIN.

IN the course of an investigation (*J. Agric. Sci.*, 1924, in the press) on the interaction between acid soils and calcium carbonate, unsatisfactory results were given by the ordinary text-book methods for the estimation of total or free carbonic acid in dilute solutions of calcium bicarbonate. The bicarbonate concentration can be readily estimated by titration with acid to the methyl-red end-point in boiling solution. The estimation of free carbonic acid by titration with sodium carbonate solution to a permanent pink colour with phenolphthalein gave impossibly low results. In a theoretical treatment Johnstone (*J. Amer. Chem. Soc.*, 1916, **38**, 947) has shown that this estimation is unsound. It was therefore necessary to determine the total carbonic acid and obtain the free carbonic acid by difference. Treadwell and Hall ("Quantitative Analysis," 5th Edn., Vol. 2, p. 591) state that "total carbonic acid can be estimated by treat-

ment with an excess of barium chloride and barium hydroxide, and titration of the excess of the latter with hydrochloric acid using phenolphthalein as indicator," and add that the barium chloride is necessary only if alkali bicarbonates are present. Johnstone (*loc. cit.*) has shown from a consideration of the equilibrium constants of the reactions that this method can give accurate results for solutions containing only alkali metals. From the approximate equality of the solubility products of calcium and barium carbonates (Johnstone, *J. Amer. Chem. Soc.*, 1915, **37**, 200), calcium hydroxide should behave like barium hydroxide.

For calcium bicarbonate solutions it was found that either hydroxide alone gave low and erratic results. The precipitated carbonate was extremely finely divided and dissolved steadily throughout the titration, which gave no definite end-point. In many cases the solutions were completely clear before the phenolphthalein was decolorised. In the presence of an excess of the corresponding chloride, both hydroxides gave precipitates which coagulated rapidly to bulky sediments. This flocculation was, however, reversible, since on shaking during the titration the precipitates were broken up and partly dissolved, the end-points being indefinite. With increased periods of standing before titration, higher values were obtained, but the duplicates showed poor agreement even after standing for 3 hours. It appeared that the freshly-formed calcium carbonate was more soluble and more hydrolysed than the older precipitate or calcite. An attempt was made to "age" the precipitate more rapidly by seeding the solutions with powdered calcium carbonate, so as to provide nuclei on which that formed by the reaction might deposit in a compact and less soluble form. Such solutions gave fairly well-defined end-points after standing for only a few minutes and constant results after about 10 minutes.

Typical comparisons of six methods with different periods of standing are given below for a calcium bicarbonate solution (A) of known total carbonic acid content, and for a hard tap-water (B).

Experimental.

The bicarbonate solution was prepared by the action of hydrochloric acid on an excess of calcium carbonate in a bottle completely filled by the solution, with a corresponding bottle without acid for the blank. Carefully boiled-out distilled water was taken for the blank in the experiments with tap-water. In each case 75 c.c. of solution were transferred with a minimum exposure to the air to stoppered bottles containing 30 c.c. of the alkaline solutions prepared, as indicated, from *N*/25-barium or calcium hydroxide

with 10 c.c. of 10 per cent. solution of the corresponding chloride and about 0·2 gm. of pure calcium carbonate which had been previously well washed and dried. After varied periods of standing, the titrations were carried out slowly with $N/20$-hydrochloric acid to the point at which phenolphthalein was decolorised. In the solutions containing calcium carbonate there was a very slow return of the pink colour, but no difficulty was experienced in defining to one drop the point at which the decoloration persisted for several minutes. The calcium bicarbonate solution contained 7·5 c.c. and the tap-water 8·0 c.c., of $N/20$-bicarbonate.

Total Carbonic Acid in c.c. $N/20$.

Hours standing.	$Ba(OH)_2$.	$Ba(OH)_2$ $+BaCl_2$.	$Ca(OH)_2$.	$Ca(OH)_2$ $+CaCl_2$.	$Ca(OH)_2$ $+CaCO_3$.	$Ca(OH)_2$ $+CaCl_2$ $+CaCO_3$.
A. Calcium bicarbonate solution containing 16·45 c.c. of $N/20$-total carbonic acid.						
0·3	0·4	4·9	5·8	8·2	15·5	16·1
0·6	1·7	8·4	8·9	11·8	15·7	15·7
1·0	4·0	9·3	11·0	13·6	16·0	16·4
1·0	1·2	13·0	11·6	15·2	16·8	16·6
3·0	9·5	14·8	14·9	16·0	15·7	16·3
3·0	5·7	13·5	15·9	15·8	16·7	16·5
B. Tap-water.						
0·3	0·4	11·8	1·7	3·3	12·8	13·7
0·6	0·4	13·1	3·2	6·8	12·8	13·6
1·0	1·2	12·3	9·3	10·7	13·0	13·7
3·0	11·8	12·3	12·4	12·8	13·2	13·8

The table clearly shows the failure of the usual methods and the increased speed and accuracy resulting from the addition to the calcium hydroxide and chloride solution of a small amount of solid calcium carbonate.

ROTHAMSTED EXPERIMENTAL STATION,
HARPENDEN.

[*Received, June 17th*, 1924.]

CCXLVIII.—*The Rotatory Dispersion of Derivatives of Tartaric Acid. Part I. Methylene Derivatives.*

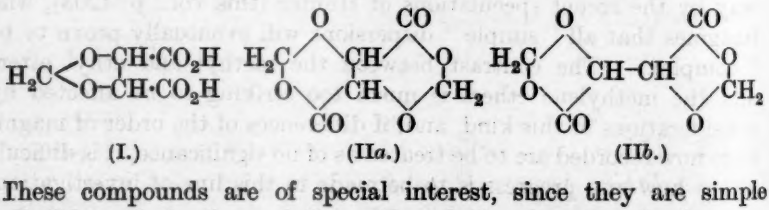
By PERCY CORLETT AUSTIN and VICTOR ALEXANDER CARPENTER.

IT has been known for nearly a century that aqueous solutions of tartaric acid exhibit in an extreme form the property of anomalous rotatory dispersion. The anomalies persist in an equally extreme form in the simple esters; but a few derivatives have already been found (Lowry and Austin, *Phil. Trans.*, 1922, *A*, 222, 249) in which they disappear so completely that the rotatory dispersion becomes

not only *normal* but *simple*, in the sense that *the observed rotations can be expressed by one term of Drude's equation, not only in the visible region of the spectrum but also in the ultra-violet, up to the limit of transparency, within which alone Drude's equation is valid.* In seeking the origin of the anomalous rotatory dispersion of the acid, special interest attaches to the discovery of cases of the latter type, two of which are described in this paper, namely, the mono- and di-methylene derivatives which result from an interaction between tartaric acid and formaldehyde.

The starting point for our work was the interesting observation of Lobry de Bruyn and van Ekenstein (*Rec. trav. chim.*, 1902, **21**, 313) that when a mixture of tartaric acid, formalin, and sulphuric acid is kept for six weeks the dextrorotatory acid yields a lævorotatory solution, although in the absence of sulphuric acid the dextrorotation is increased by the addition of formaldehyde. It appeared likely that a fuller investigation of this reaction might throw light upon the origin of the reversal of sign (*e.g.*, as a result of changes of solvent or of concentration) which is associated with the anomalous rotatory dispersion of the acid. This belief was strengthened when we found that a mixture of tartaric acid and formalin in solution exhibited an unmistakable mutarotation; indeed, this observation indicated clearly that the changes of rotatory power were due to the occurrence of a chemical change in the solution, and not to any merely physical change, the effects of which would be manifested immediately without any lag beyond that covered by adjustments of temperature, etc.

The two compounds which we have prepared and examined are the *lævorotatory* methylene-ether of formula I and the *dextrorotatory* ether-ester, to which the formula IIa or IIb must be assigned.



(I.) (II*a*.) (II*b*.)

These compounds are of special interest, since they are simple alkylidene derivatives of the acid and therefore are closely comparable with the alkyl esters in many of their properties. Now, in absorption spectroscopy, a general rule has been established that alkylation has no notable influence on the optical properties of a compound *unless it is accompanied by a change of structure.* Since there is a profound difference in the behaviour and optical properties of the free acid and its esters on the one hand, and of the alkylidene derivatives on the other hand, it is clear that whilst the acid and its

esters have a comparable structure some novel structural feature has been developed in the alkylidene compounds which influences their optical properties profoundly. This novel effect may be due to the fact that, in the esters, only the *carboxylic hydrogen atoms* of the acid have been displaced, whilst in the methylene derivatives the *hydroxylic hydrogen atoms* have disappeared, but we are not yet prepared to assert that the elimination of the hydroxylic hydrogens is in itself sufficient to remove the optical anomalies of the acid, since the development of ring systems may also play a decisive part in producing " simple " rotatory dispersion in the methylene derivatives.

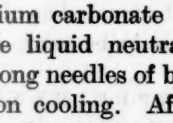
In addition to the sudden and complete change from complex and anomalous rotatory dispersion to " simple " dispersion (as defined above), the formation of the methylene derivatives is accompanied by the development of exceptionally high rotatory powers, as compared with those of the acid and its esters, and by the disappearance of the sensitiveness to changes of solvent and of concentration which Biot regarded as one of the chief anomalies of tartaric acid. Thus the specific rotations of methylene tartaric acid are not altered by changing the concentration from 6 to 32 per cent., whilst the dimethylene derivative has practically the same rotatory power in acetone as in ethyl acetate. In each case the constancy of rotatory power persists throughout the whole range of the spectrum covered by our observations. It is difficult to resist the conclusion that the *flexibility* of the rotations and the *anomaly* of the rotatory dispersion arise from a common cause, and that their simultaneous disappearance is due to the fixing of a structure which is still plastic in the acid and its esters. We may add that the experiments described in this paper and the conclusions drawn from them are not affected in any way by the recent speculations of Hunter (this vol., p. 1203), who imagines that all " simple " dispersions will eventually prove to be " complex." The contrast between the methyl and ethyl esters and the methylene ethers is much too striking to be affected by considerations of this kind, and, if differences of the order of magnitude now recorded are to be treated as of no significance, it is difficult to see how any progress is to be made in this line of investigation.

Experimental.

Interaction of Paraformaldehyde and Tartaric Acid.—When these substances are melted together and concentrated sulphuric acid is added to the cooled mixture, both the mono- and the di-methylene derivatives are formed. The latter is readily separated and purified, but the isolation of the former is somewhat difficult and the values recorded in the literature for its melting point and specific rotation

are too low (Henneberg and Tollens, *Annalen*, 1896, **292**, 53, give m. p. 138—140° for the hydrate containing $2H_2O$; Lobry de Bruyn and van Ekenstein, *loc. cit.*, give, for the anhydrous acid, m. p. 160° and $[\alpha]_D = -73°$ in 0·8 per cent. aqueous solution). The hydrated and anhydrous forms have m. p. 140·5° and 165°, respectively, and the latter has $[\alpha]_D^{20°} - 81·3°$.

Barium Methylene Tartrate.—Powdered tartaric acid (100 gms.) mixed with 2 c.c of water (to depress the melting point) was heated at 165°, and paraformaldehyde (30 gms.) was added in small portions; when the mixture became quite liquid on stirring, the temperature was lowered to 155°. The mixture was allowed to cool slowly to 60° and pure sulphuric acid (70 gms.) added, care being taken to keep the temperature below 70°. Water (200 c.c.) was added and the mixture boiled. Extraction by benzene of the dimethylene tartrate at this stage, although recommended by Lobry de Bruyn and van Ekenstein, was omitted, as this ester is only slightly soluble in cold benzene. Barium carbonate (136 gms.) was stirred into the boiling solution. This amount was slightly in excess of that required to precipitate the sulphuric acid. It was a distinct advantage to filter this off before neutralising the organic acids. The clear filtrate was then boiled again and neutralised by adding a thin paste of barium carbonate (135 gms.) and water. Barium tartrate was filtered off and the solution concentrated by boiling. This process was accompanied by the separation of further crops of barium tartrate. At the same time, a strong odour of formaldehyde was noticed and the liquor became strongly acid. This was evidently due to the gradual hydrolysis of dimethylene tartrate to formaldehyde and tartaric acid, which in its turn reacted with the soluble barium methylene tartrate. Lobry de Bruyn and van Ekenstein held, on the other hand, that this behaviour proved the presence of an unstable, unsymmetrical monomethylene monobasic acid for which the structure $\begin{matrix} O\text{—}CO \\ | \\ CH_2\text{—}O \end{matrix}\!>\!CH\cdot CH(OH)\cdot CO_2H$ was suggested, but there is no other evidence of the existence of such a compound.* During the evaporation, more barium carbonate was added from time to time in order to keep the liquid neutral. From the hot, concentrated, filtered solution long needles of barium methylene tartrate (43 gms.) were deposited on cooling. After recrystallisation 3 or 4 times from hot water (to free them from barium tartrate) they were obtained pure. The salt is extremely hygroscopic, a fact which

* The alternative structure  was evidently overlooked by these authors.

rendered the subsequent extraction of the free acid somewhat tedious, as each sample that was used had to be analysed separately (for barium) before the exact amount of sulphuric acid needed for its decomposition could be calculated.

1·8493 gave 1·1884 $BaSO_4$. Ba = 37·82. 0·4758 lost 0·0850 at 102°. H_2O = 17·86. Hence Ba in anhydrous salt = 46·04 ($C_5H_4O_6Ba$ requires Ba = 46·19 per cent.).

Methylene Tartaric Acid (I).—The barium salt was decomposed by boiling 2*N*-sulphuric acid (calc. amount). The aqueous solution of the pure acid obtained after filtration was used for some of the polarimetric readings, the strength being determined by titration against 0·2*N*-caustic potash (standardised against pure tartaric acid). But in order to make doubly sure of the accuracy of the readings, the acid was isolated by evaporating the solution almost to dryness, when crystals were obtained which melted at 140·5° when dried in the desiccator and at 162° when dried at 100°; on long standing in the desiccator, the melting point rose to 165°. The acid is very hygroscopic and very soluble in water. The solutions in water are strongly lævorotatory and the rotatory dispersion can be expressed by one term of Drude's equation. The specific rotation is practically independent of concentration for all wave-lengths. The solutions are not decomposed by boiling. A solution of this compound in water gave the same values for the specific rotations as the solution prepared from the barium salt. 0·5322 required 32·9 c.c. of 0·1982 *N*-KOH; 1·0825 lost 0·0040 at 100°. Hence equiv. wt. of the anhydrous acid = 81·31. $C_5H_6O_6$ requires 81·00. It is therefore dibasic and must have the structure assigned to it.

Rotatory power and rotatory dispersion of the acid were determined in aqueous solutions containing 31·93 gms. and 6·288 gms. of the anhydrous acid in 100 c.c. in a 4-dcm. tube. In addition to the quartz mercury-vapour lamp, open arcs with electrodes of copper and of cadmium–silver alloy were used. Additional readings were obtained by the photographic method. The polarimeter was made by Messrs. Bellingham and Stanley. Results are set forth in Table I.

Dimethylene Tartrate, $C_6H_6O_6$.—This compound was prepared by the method described in the German patent specification (D.R.-P. 1901, No. 130346. E. Schering). Powdered tartaric acid (70 gms.) mixed with 2 c.c. of water was heated at 150° and paraformaldehyde (30 gms.) stirred in. On cooling, concentrated sulphuric acid (150 gms.) was added and the mixture poured into ice-cold water (300 c.c.), when crystals of the ester were precipitated. When dried in the vacuum desiccator, the crystals weighed 35 gms. The substance was purified by recrystallising twice from benzene, after which

TABLE I.

Rotatory Dispersion of Methylene Tartaric Acid in Aqueous Solution at 20°.

(*a*) First series. 28·38 Gms. of $C_5H_6O_6$ in 100 gms. of solution or 31·93 gms. in 100 c.c.

Density = 1·1251. *Length of tube* = 4 dcm.

Simple formula $[\alpha_1] = \frac{-24{\cdot}627}{\lambda^2 - 0{\cdot}0446}$.

λ.	α.	[α] obs.	[α$_1$] calc.	[α]−[α$_1$].
Cu 5782	−108·12°	− 84·66°	− 85·00°	+0·34°
Hg 5780	−108·59	− 85·03	− 85·07	+0·04
Cu 5700	−112·22	− 87·87	− 87·86	−0·01
Hg 5461	−124·01	− 97·10	− 97·10	±
Cu 5219	−137·79	−107·90	−108·11	+0·21
Cu 5154	−142·21	−111·35	−111·41	+0·06
Cu 5105	−145·67	−114·06	−114·01	−0·05
Cd 5086	−146·98	−115·08	−115·04	−0·04
Cd 4800	−169·44	−132·67	−132·54	−0·13
Fe 4737	*−176*	*−137·8*	*−137*	*−0·8*
Hg 4359	−216·28	−169·36	−169·36	±
Fe 4096	*−256*	*−200·5*	*−200·0*	*−0·5*
Fe 3978	*−276*	*−216·0*	*−216·7*	*+0·7*
Fe 3879	*−296*	*−231·8*	*−232·6*	*+0·8*

(*b*) Second series. 6·145 Gms. of $C_5H_6O_6$ in 100 gms. of solution or 6·288 gms. in 100 c.c.

Density 1·0233. *Length of tube* 4 *dcm.*

Simple formula $[\alpha_1] = \frac{-24{\cdot}662}{\lambda^2 - 0{\cdot}04356}$.

λ.	α.	[α] obs.	[α$_1$] calc.	[α]−[α$_1$].
Cd 6438	−16·71°	− 66·43°	− 66·48°	+0·05°
Na 5893	−20·45	− 81·30	− 81·20	−0·10
Cu 5782	−21·33	− 84·80	− 84·82	+0·02
Hg 5780	−21·38	− 85·00	− 84·89	−0·11
Cu 5700	−22·15	− 88·06	− 87·63	−0·43
Ag 5469	−24·22	− 96·29	− 96·51	+0·22
Hg 5461	−24·36	− 96·84	− 96·84	±
Cu 5219	−27·08	−107·66	−107·78	+0·12
Ag 5209	−27·29	−108·49	−108·27	−0·22
Cu 5154	−27·86	−110·76	−111·05	+0·29
Cu 5105	−28·63	−113·82	−113·62	−0·20
Cd 5086	−28·90	−114·89	−114·65	−0·24
Cd 4800	−33·23	−132·10	−132·00	−0·10
Cd 4678	−35·25	−140·14	−140·70	+0·56
Hg 4359	−42·36	−168·40	−168·40	±
Fe 4046	*−52*	*−206·7*	*−205·3*	*−1·4*
„ 3978	*−54*	*−214·7*	*−215·0*	*+0·3*
„ 3879	*−58*	*−230·6*	*−230·7*	*+0·1*
„ 3720	*−65*	*−258·4*	*−260·0*	*+1·6*

Table II.

Rotatory Dispersion of Dimethylene Tartrate in Ethyl Acetate at 20°.

9·80 gms. of $C_6H_6O_6$ in 100 c.c. Length of tube 2 dcm.

$$\textit{Simple formula } [\alpha_1] = \frac{+34{\cdot}168}{\lambda^2 - 0{\cdot}03132}.$$

	λ.	α.	[α] obs.	[α$_1$] calc.	[α]−[α$_1$].
Cd	6438	+17·58°	+ 89·7°	+ 89·2°	+0·5°
Zn	6364	17·89	91·3	91·4	−0·1
Na	5893	21·14	107·9	108·1	−0·2
Cu	5782	22·14	112·9	112·7	+0·2
Hg	5780	22·15	113·0	112·9	+0·1
Cu	5700	22·78	116·2	116·4	−0·2
Hg	5461	25·09	128·0	128·0	±
Cu	5219	27·75	141·6	141·7	−0·1
Ag	5209	27·83	142·0	142·3	−0·3
Cu	5154	28·59	145·9	145·8	+0·1
Cu	5105	29·29	149·4	149·0	+0·4
Cd	5086	29·42	150·1	150·2	−0·1
Zn	4811	33·45	170·7	170·7	±
Cd	4800	33·80	172·4	171·6	+0·8
Cd	4678	35·60	181·6	182·2	−0·6
Hg	4359	42·20	215·3	215·3	±
Fe	*4251*	*45*	*229·6*	*228·7*	+0·9
,,	*4144*	*48*	*244·9*	*243·3*	*+1·6*
,,	*4096*	*49*	*250·0*	*250·4*	−0·4
,,	*3860*	*57*	*290·8*	*290·4*	+0·4
,,	*3720*	*63*	*321·4*	*319·1*	+2·3

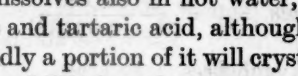
Table III.

Rotatory Dispersion of Dimethylene Tartrate in Acetone at 20°.

5·10 gms. of $C_6H_6O_6$ in 100 c.c. Length of tube 4 dcm.

$$\textit{Simple formula } [\alpha_1] = \frac{+34{\cdot}405}{\lambda^2 - 0{\cdot}0311}.$$

	λ.	α.	[α] obs.	[α$_1$] calc.	[α]−[α$_1$].
Cd	6438	+18·37°	+ 90·0°	+ 89·7°	+0·3°
Zn	6364	18·62	91·3	92·0	−0·7
Na	5893	22·20	108·8	108·8	±
Cu	5782	23·15	113·5	113·5	±
Hg	5780	23·15	113·5	113·6	−0·1
Cu	5700	23·89	117·1	117·1	±
Ag	5469	26·20	128·5	128·4	+0·1
Hg	5461	26·21	128·5	128·8	−0·3
Cu	5219	29·12	142·7	142·6	+0·1
Ag	5209	29·31	143·7	143·2	+0·5
Cu	5154	29·91	146·6	146·7	−0·1
Cu	5105	30·56	149·8	149·9	−0·1
Cd	5086	30·86	151·3	151·2	+0·1
Zn	4811	35·10	172·1	171·7	+0·4
Cd	4800	35·31	173·1	172·6	+0·5
Zn	4722	36·54	179·1	179·3	−0·2
Hg	4359	43·98	215·6	216·5	−0·9
Fe	*4202*	*48·1*	*236*	*236·5*	−0·5
,,	*4135*	*50·1*	*246*	*246*	±
,,	*4072*	*52·1*	*255*	*255*	±

it melted sharply at 119°. It dissolves at the ordinary temperature in dry acetone, ethyl acetate, or formamide, but in alcohol, benzene, chloroform, ethylene dibromide, acetylene tetrachloride, or tetrachloroethane it dissolves only when heated, and it crystallises on cooling. It dissolves also in hot water, but is slowly hydrolysed to formaldehyde and tartaric acid, although if the hot aqueous solution be cooled rapidly a portion of it will crystallise out. Two alternative formulæ (IIa and IIb) have been suggested to represent its structure. The possibility of such a configuration as  is ruled out on the grounds that (i) the formation of a 7-membered ring is improbable and (ii) such a compound would be easily hydrolysed to form the stable lævorotatory monomethylene tartaric acid; but the evidence is not yet sufficient to decide between the formulæ IIa and IIb.

Dimethylene tartrate is a neutral ester, but on prolonged boiling with water it is hydrolysed to a dextrorotatory dibasic acid. 1·8130 gms., boiled with water for 2½ hours, gave an acid solution from which crystals no longer separated on cooling. 105·5 c.c. of 0·1978 *N*-baryta were required to neutralise it. Equiv. wt. = 86·96 ($C_6H_6O_6$ requires equiv. wt. = 87·0 if a dibasic acid is produced).

The rotatory power and the rotatory dispersion of the ester were measured in solutions in dry acetone and in dry ethyl acetate. The solutions were dextrorotatory and the dispersion can be expressed by one term of Drude's equation. The specific rotation appears to be practically independent of concentration and of solvent. The results are set forth in Tables II and III.

We desire to express our indebtedness to the Government Grant Committee of the Royal Society for a substantial grant for the purchase of the necessary apparatus. We are also indebted to Prof. T. M. Lowry, C.B.E., F.R.S., for the interest which he has taken in the investigation.

WESTMINSTER TRAINING COLLEGE,
130, HORSEFERRY ROAD, S.W. 1.

[*Received, February 22nd,* 1924,
Revised, August 21st, 1924.]

CCXLIX.—*A New Method of Micro-gas Analysis.*

By LEWIS REEVE.

DURING the course of an investigation upon the photo-decomposition of aqueous solutions of oxalic and formic acids by ultra-violet light, it became necessary to devise methods for the quantitative examination of the extremely small quantities of gases produced. The

most complex of these gas mixtures consisted of carbon dioxide, carbon monoxide, hydrogen, and formaldehyde; their volumes averaged about 0·05 c.c. at *N.T.P.*, but were often far smaller.

An account is now given of the methods which were adopted for the measurement and analysis of these mixtures to within about 0·5 per cent. of their volumes, and of such mixtures, containing a gaseous hydrocarbon (*e.g.*, methane); also a method is suggested for the direct analysis of any oxygen present.

Nearly all the very few methods of micro-gas analysis devised hitherto depend on the measurement, by means of some form of accurate manometer or McLeod gauge, of the low pressures exerted by the gas mixture in a constant volume of fair magnitude (Guye and Germann, *Compt. rend.*, 1914, **159**, 154; Ryder, *J. Amer. Chem. Soc.*, 1918, **40**, 1656; Shearer, *Phil. Trans.*, 1922, *B*, **193**, 213).

None of these methods was employed; instead the simpler process of measuring the gas at atmospheric pressure in a calibrated capillary tube was adopted; a process which, after certain sources of error were removed, gave perfectly consistent results. Timiriazeff (*Ann. Chim. Phys.*, 1877, [v], **12**, 355) employed a rather complex apparatus, based upon this principle, for the analysis of small quantities of gas mixtures of carbon dioxide and oxygen, but no other work on the subject has been published. The greater part of the following apparatus and the analytical method as a whole are, as far as is known to the author, entirely new.

The Measuring Tube.—The apparatus (Fig. 1) for measuring the gases collected gave reproducible results with even the tiniest quantities. It consisted of a calibrated, uniform, fine-bore capillary tube, *BAP*, bent as shown. The U-shaped portion, *L*, was employed as a gas-siphon and was drawn off to a fine point which, normally, dipped a few millimetres below the surface of the mercury in the jar, *C*. The straight portion, *HK*, was about 40 cm. in length; the remaining dimensions can be judged from the diagram, which is roughly to scale. The bore of the capillary used was such that 1 mm. length of the tube represented 0·000547 c.c., *i.e.*, a bore of approximately 0·8 mm.; but this could be increased or decreased within limits, if required. The tube was provided with a rubber connecting tube, a small reservoir of mercury, *R*, a screw clip, *D*, normally closed, and a jacketing tube, *G*. The last was used as an amyl alcohol jacket in certain experiments to be described later, whilst it could also be used, if necessary, as a constant temperature water jacket. However, the accuracy of the work for which the measuring tube was employed did not justify the latter refinement and, normally, the jacket was left empty, all measurements being carried out at room temperature. Three small, drawn-out

bulbs, *E*, *F*, and *W*, internal diameter about 3 mm. and volume about 0·05 c.c., the uses of which will be described later, were blown at the positions shown. The jacketed portion of the tube, in which the actual measurements were carried out, was provided with a glass scale (a thermometer tube provides an excellent substitute for this).

FIG. 1.

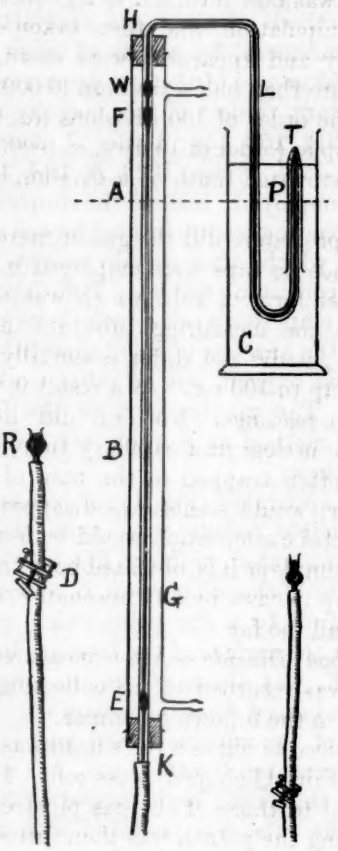
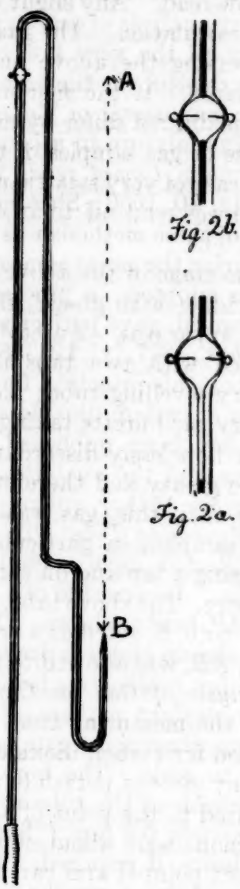


FIG. 2.



Finally, the whole apparatus was mounted on a suitable stand (not shown in the sketch).

The method of using the tube is almost obvious. The gases to be measured were collected from a Töpler pump and stored over mercury in a small collecting tube, about 7 mm. in diameter and 7 cm. long, the closed end being drawn out somewhat. This collecting tube was transferred in a crucible of mercury to the jar,

C, and the gas, with a following thread of mercury, was completely sucked into the measuring tube in the customary way. The thread of gas, *AB*, was now brought to the atmospheric pressure by bringing *A* to a point, found by trial to be proper, slightly above that indicated in Fig. 1, then removing the jar, *C*, and adjusting the reservoir to bring *A* and *P* to the same level. The volume of gas was now read. Any slight error in levelling *A* with *P* was allowed for by calculation. The gas was now returned to its collecting tube by reversing the above manipulation, and then taken back and remeasured. If the mercury and apparatus were clean, the two readings did not differ by more than half a division (0·00027 c.c.) in the case of gas samples of the order of 100 divisions (*ca.* 0·05 c.c.). In the case of very small samples (order of 10 divs. = 0·005 c.c.), the volume was read off to an estimated tenth of a division by using a pocket lens.

At no stage of the above procedure did the gas or mercury come into contact with grease, since no taps were employed in any part of the apparatus. An earlier form of tube which was tested was provided with two taps in the measuring tube and a separate capillary levelling tube; *i.e.*, it did not differ essentially from the ordinary gas burette taking up to 100 c.c. As a result it was found to give hopelessly discordant readings. Not only did the mercury become greasy and therefore useless in a capillary tube, but, more serious than this, gas was often trapped in the bore of the taps. Small samples, in particular, would sometimes disappear entirely on passing a tap and on careful examination would be found lodged in its bore. The above tube, simple as it is, obviated both these errors.

The bulb, *E*, acted as a trap in case, by any mischance, the thread of gas, *AB*, was allowed to fall too far.

Analysis of Gas for Carbon Dioxide.—After measurement, the gas in the measuring tube was returned to the collecting tube and analysed for carbon dioxide in the following manner.

A tiny piece of potash (a piece as big as a pin's head was sufficient) was fused to the point of a thin, U-shaped, glass rod. The latter's dimensions were about equal to those of the gas pipette in Fig. 1. Its short pointed arm carrying the potash was then introduced into the collecting tube containing the gas and left there for a short time; half an hour was more than sufficient. Any carbon dioxide in the gas was thus entirely absorbed. The rod was then removed, the greatest care being taken that the point, as it disappeared below the surface of the mercury, did not touch the side of the tube; otherwise some of the residual gas was dragged down with it. This residue was then measured in the measuring tube and the amount of carbon dioxide in the original gas calculated. "Blank" experiments

carried out on pure oxygen, with the potash applied in this way, showed that the loss of gas was negligible, provided the piece of potash was small.

When not in use, the glass rod, with its potash-covered point, was immersed in mercury, out of contact with the atmosphere. It was used for a few determinations and then renewed.

Proposed Method for Direct Analysis of Oxygen.—Although the method has not been tested, there seems to the author no reason why oxygen should not be estimated in a manner similar to that described above for carbon dioxide, using phosphorus instead of potash on the point of the glass rod.

Analysis for Carbon Monoxide and Hydrogen.—This was carried out by explosion with oxygen. Here again various causes of error had to be removed before accurate results could be obtained. A small eudiometer tube was first used, with platinum electrodes fused in as high as possible in its head. It was found, however, that owing to, apparently, the proximity of the spark to the comparatively large mercury surface in such a tube, with consequent oxidation, an appreciable loss of oxygen (as much as 5 divs.) could occur, even as the result of the passage of a single spark. Further, quantities of gas smaller than 60 divs. (*ca.* 0·03 c.c.) could not be sparked at all, it being impossible to make a eudiometer tube to take them. The eudiometer was replaced, therefore, by an apparatus in which the gases were exploded in an explosion bulb with capillary ends. Two such explosion tubes were used, one for dealing with quantities of gas of the order of 100 divs. and another, working under reduced pressure, for very small quantities—of the order of 10 divs.

The larger explosion tube was at first a separate piece of apparatus, but it was later incorporated with the measuring tube already described (Fig. 1). A known volume of gas, after analysis for carbon dioxide, was mixed with a known volume of oxygen and introduced into the tube until it occupied the space of the bulb, *F* (Fig. 1); here it was sparked. Platinum electrodes, passing through the walls of the bulb, were formerly employed for this purpose. It was found, however, that there was really no need for these, since they could be replaced by the two mercury surfaces bounding the bubble of gas on either side. For this purpose, one wire from the ignition coil used as the source of spark was allowed to dip in the mercury in the reservoir, *R*, and the other in the mercury in the jar, *C*. No appreciable loss of oxygen was found to occur as a result of using the mercury surfaces as electrodes in this way; their area, it should be remembered, was extremely small, since they were only just projecting from the capillary ends of the bulb.

After explosion, the reduction in volume and the amount of

carbon dioxide formed were determined, and from these data the amounts of hydrogen and carbon monoxide in the original gases were calculated in the usual manner, allowance being made for the pressure of aqueous vapour.

Explosion under Reduced Pressure.—Apart from the difficulty of making a bulb small enough to explode quantities of gas as small as 10 divs. (*ca.* 0·005 c.c.), it seemed probable that the loss of oxygen in such a bulb might become appreciable. Hence, as already mentioned, for the explosion of such extremely small quantities a special tube was employed, in which the process was carried out under reduced pressure. It consisted of a fine-bore capillary tube, bent as shown (Fig. 2), and provided with the usual gas-siphon. The length, *AB*, is 50 cm. and the remaining dimensions can be judged from the drawing, which is again roughly to scale. Near the top of the straight arm of the tube was blown a small bulb of about 0·03 c.c. capacity, through the walls of which passed two platinum electrodes. For various reasons, which need not be discussed here, it was found to be inconvenient, although not impossible, to use the mercury as electrodes for this bulb. A mercury reservoir was connected, by means of a rubber tube, to the same arm, as shown, and the usual screw clip was provided. The gas to be sparked was drawn into the tube in the usual manner and as it reached the bulb its pressure was reduced and it expanded to about four times its volume at atmospheric pressure. The result was that it could be sparked with ease, nor was there any loss of oxygen.

The maximum volume of gas which could be sparked in this apparatus, used as described above, was 15 divs. (*ca.* 0·0075 c.c.), measured at atmospheric pressure. This meant that as small a quantity as 2 divs. (0·001 c.c.) of carbon monoxide or hydrogen could be detected and measured with some degree of accuracy. The apparatus could be used, however, for sparking larger volumes than 15 divs. by placing a rubber stopper over the point of the gas-siphon, with the mercury reservoir in such a position that the mercury was just entering the bulb at the top (Fig. 2*a*). By then raising the mercury reservoir until mercury began to enter the bulb at the bottom (Fig. 2*b*), the gas was put into the correct position for sparking. It could not, of course, be completely burnt while some of it was still in the capillary owing to the well-known effect of such tubes of retarding explosion.

It need scarcely be pointed out that the above explosion tube could easily be incorporated with the measuring tube of Fig. 1, thus making one single piece of apparatus for measuring the gases, exploding them at the ordinary pressure, exploding them at reduced pressure, or exploding them at 130° (see below).

Analysis of Gas for Formaldehyde.—Formaldehyde gas, on continued sparking in the above apparatus, either at atmospheric or at reduced pressure and in the absence of oxygen, decomposed into carbon monoxide and hydrogen, with a consequent increase in volume, which gases could then be analysed in the usual manner. This provided a method for analysing any formaldehyde present in the gases simultaneously with carbon dioxide, carbon monoxide, and hydrogen.

Analysis of Gases for Hydrocarbons.—It is obvious that the methods already described would be insufficient for the analysis of any hydrocarbon gas, such as methane, present simultaneously in the gas mixture with carbon monoxide and hydrogen. The contraction in volume on explosion with oxygen and the amount of carbon dioxide formed provide only two equations for the solution of three unknown quantities. A third equation is obviously necessary. This, in large-scale analysis, is provided by making use of a process of fractional combustion, a process which would be difficult to carry out on a small scale. It seemed, however, that this third equation could be obtained by exploding the gases, not only at room temperature, when practically all the water formed was condensed, and noting the change in volume, but also at a temperature above 100°, when any water formed would not be condensed, thus obtaining an entirely different change in volume.

The author has had no opportunity to test the reliability of data obtained in this way for an actual mixture of methane, carbon monoxide, and hydrogen. Instead, the combustion of hydrogen alone was examined. This gas, on explosion with oxygen, at room temperature, should give a contraction of one and a half times its own volume; whilst at high temperatures it should give one of only half its own volume.

The results actually obtained, using amyl alcohol vapour in the high-temperature jacket, *G*, of Fig. 1, confirmed these conclusions. The following are some observed figures (scale divisions) compared with the calculated contractions:

Obs. contrn. at 130°	42·0	45·5	43·5	48·0
Calc. „ „	43·7	45·2	43·1	46·7
Obs. „ 16°	—	97·5	92·0	100·5
Calc. „ „	—	97·5	92·1	100·8

The experimental error in the case of the high-temperature contractions is somewhat higher than in the case of those at room temperature, but the possible sources of error are also greater (*e.g.*, varying b. p. of the amyl alcohol in the jacket 128—130°).

The following sources of error had to be removed before figures of the above accuracy could be obtained:

(*a*) The measuring tube and explosion bulb had to be perfectly dry before each determination was carried out. For this reason the tube was emptied from mercury between each determination and a current of dry air aspirated through it with the high temperature jacket in action. The dryness of the tube was then tested by introducing into it, at room temperature, the gas sample to be exploded, heating it with the jacket, and noting the increase in volume. If this was greater than Charles's law warranted, it was obvious that the tube was not perfectly dry.

(*b*) Another bulb, *W*, was needed above the true explosion bulb, *F* (Fig. 1), in order to contain a supply of hot mercury. Otherwise, when the residual gases after explosion at high temperatures (consisting largely of steam) were lowered into the capillary portion of the tube, for measurement, cold mercury entered the tube and apparently brought about some condensation. Before this bulb, *W*, was provided, the observed contractions at high temperatures were always much too great. This was particularly the case in some earlier experiments when steam, instead of amyl alcohol vapour, was used in the hot jacket. Very poor results were obtained in these experiments, and it is possible that, in addition to the above source of error, surface condensation on the walls of the capillary also occurred. (See, in this connexion, the work of Menzies on the vapour density of steam, *J. Amer. Chem. Soc.*, 1921, **43**, 851). The extra bulb, *W*, also prevented a mishap which had occurred before it was introduced, of the gas, at the instant of explosion, being driven out of the hot explosion bulb into the cold portion of the capillary above it, just outside the hot jacket. This, of course, brought about condensation of steam and, again, too large a contraction.

(*c*) A final, much smaller source of error was found to be the slight change in pressure which occurred as a result of the expansion by heat of the 0·1 c.c. of mercury in the explosion bulbs. Thus, if a gas sample were measured at the ordinary temperature and pressure (*i.e.*, with *A* and *P* of Fig. 1 on the same level), then, on heating, as a result of the expansion of the mercury, a slight difference in level, with a corresponding increase in pressure, would be set up between *A* and *P*. It should be noted that this increase in pressure was not compensated by the decrease in density of the hot mercury. The correction necessary for this increase amounted to less than 1 per cent. of the gas volume.

It can easily be shown that the effects of difference in temperature on the bore of the capillary and on the surface tension of mercury (both of which, if appreciable, would affect the measurements) are quite negligible.

From the results shown in the table on p. 1952, there seems little reason to doubt that the method described would give trustworthy results in practice, enabling, therefore, a hydrocarbon gas to be determined in admixture with the other gases.

Test of the Accuracy of the above Methods of Analysis.—Apart from the consistency of the above and numerous similar results, the accuracy of the methods was finally tested by analysing a gas mixture containing carbon dioxide, carbon monoxide, and hydrogen, using first samples of 100 c.c. and ordinary Hempel gas-analysis apparatus (filled with acidified water) and then samples of the same gas averaging 0·03 c.c. in volume and the above apparatus and methods of micro-gas analysis. The means of three experiments in each case are given in the following table:

	CO_2.	CO.	H_2.
Large scale (100 c.c.) ...	2·9	42·3	33·4%
Micro-scale (0·03 c.c.) ...	2·8 (determined on 0·1 c.c.)	42·5	34·0%

The experimental error in the case of the micro-samples was actually smaller than in the large-scale analyses.

Summary.

Apparatus and methods have been described for the accurate analysis of very small quantities of gas mixtures containing carbon dioxide, carbon monoxide, hydrogen, and formaldehyde. A method has also been devised which would deal with the presence of a hydrocarbon gas in such a mixture, whilst, finally, a method for the direct analysis of any oxygen present has been suggested.

The author's thanks are due to Prof. A. J. Allmand for his unstinted help and encouragement during the course of the above work, and to the Department of Scientific and Industrial Research for a grant to the author while a student in training.

KING'S COLLEGE, LONDON. [*Received, March 6th*, 1924.]

CCL.—*The Temperature Coefficient of the Quinhydrone Electrode.*

By EINAR BIILMANN and INGER KRARUP.

As the quinhydrone electrode has become useful for several kinds of electrometric measurements, a careful determination of its temperature coefficient seems desirable. Measurements of the *E.M.F.* of cells of the type

Pt|Quinhydrone, electrolyte, hydrogen (1 atm.)|Pt

at 18° and 25° are already available (Biilmann and Lund, *Ann. Chim.*, 1921, [ix], **16**, 327: Biilmann, *Trans. Faraday Soc.*, 1924, **19**, 676), so that it is necessary only to measure the *E.M.F.* of similar cells at 0° and 37° in order to obtain the potential–temperature relationship of the electrode for the temperature range 0—37°. It is now shown that, within the limits of accuracy of the experimental method, *the potential–temperature curve of the quinhydrone electrode is a straight line.*

The measurements were carried out with quinhydrone in three electrolytes: 0·1*N*-HCl; 0·01*N*-HCl, 0·09*N*-KCl; and a phosphate buffer solution of p_H 6·81. In every case, a hydrogen electrode in the appropriate electrolyte was used as standard, and the same electrolyte was employed in the connecting vessel. By this means liquid junction potentials were entirely avoided. Platinised platinum electrodes in duplicate were employed in the hydrogen electrode vessel, and blank platinum electrodes in triplicate in the quinhydrone vessel. In no case did measurements with different electrodes in the same vessel differ by more than 0·1 millivolt.

Temperature control was secured by means of water thermostats fitted with standard thermometers, and the additional precaution was taken of fitting the connecting vessel with a thermometer. Temperature equilibrium was attained at 0° and 37° within 30—45 minutes, but for the measurements at 0° it was found necessary to immerse, not only the electrode vessels, but also the siphon tubes, in ice in order to secure steady potentials.

The results are collected in Tables I—III, in which B represents the pressure of moist hydrogen at which the potentials, π, were measured, and "π corr." is the mean value of π corrected to dry hydrogen at 760 mm. of mercury. The column headed "mins." gives the time elapsing between the preparation of the quinhydrone solution and the measurement of the *E.M.F.*

TABLE I.

Pt|Quinhydrone; 0·1*N*-HCl; H_2|Pt

(for measurements at 18° and 25°, see Biilmann, *loc. cit.*).

0°: B = 777 mm.				37°: B = 777 mm.			
Mins.	π.	Mins.	π.	Mins.	π.	Mins.	π.
45	0·7173	85	0·7175	15	0·6895	55	0·6895
60	0·7174	100	0·7174	30	0·6895	70	0·6894
70	0·7175	Mean	0·7174	40	0·6895	Mean	0·6895
	π corr. 0·7172.				π corr. 0·6900.		

Table II.

Pt|Quinhydrone; 0·01*N*-HCl, 0·09*N*-KCl; H_2|Pt

(for measurements at 18°, see Veibel, J., 1923, **123**, 2203).

0° : B = 763 mm.		25·8° : B = 770 mm.		37° : B = 766 mm.	
Mins.	π.	Mins.	π.	Mins.	π.
45	0·7173	30	0·6985	15	0·6889
60	0·7173	40	0·6984	30	0·6890
80	0·7174	105	0·6983	45	0·6890
90	0·7174			55	0·6889
Mean	0·7174	Mean	0·6984	Mean	0·6890
π corr.	0·7174	π corr.	0·6986	π corr.	0·6897
		for 25°	0·6992		

Table III.

Pt|Quinhydrone; phosphate, p_H 6·81; H_2|Pt

(for measurements at 18° and 25°, see Biilmann, *loc. cit.*).

The phosphate buffer was prepared by mixing equal volumes of M/15-KH_2PO_4 and M/15-Na_2HPO_4.

0° : B = 758 mm.		37° : B = 767 mm.			
Mins.	π.	Mins.	π.	Mins.	π.
30	0·7170	15	0·6896	65	0·6893
65	0·7170	25	0·6896	95	0·6893
105	0·7170	40	0·6893	100	0·6893
150	0·7170	55	0·6892	Mean	0·6894
Mean	0·7170	π corr.	0·6801		
π corr.	0·7171				

All the above potentials are easily reproduced.

On plotting the above results, it was found that they fell practically on the straight line represented by the equation

$$\pi_t = 0{\cdot}7175 - 0{\cdot}00074t,$$

where π_t is the potential of the electrode at $t°$. Table IV shows the satisfactory agreement between the observed results and those calculated from the above equation. In no case is the discrepancy more than 0·4 millivolt.

Table IV.

		Observed potential.		
Temp.	Calc. potential.	0·1*N*-HCl.	0·01*N*-HCl, 0·09*N*-KCl.	Phosphate. p_H 6·81.
0	0·7175	0·7172	0·7173	0·7171
18	0·7042	0·7044	0·7042	0·7045
25	0·6990	0·6990	0·6992	0·6990
37	0·6901	0·6901	0·6897	0·6901

THE UNIVERSITY, COPENHAGEN.

[*Received, July 10th*, 1924.]

CCLI.—*The Influence of Nitrogen Dilution on the Speed of Flame. Part I.*

By COLIN CAMPBELL and OLIVER COLIGNY DE CHAMPFLEUR ELLIS.

THE inhibiting influence of nitrogen upon combustion is now so well known as to have become of practical use. Bunsen (*Ann. Physik.*, 1867, **131**, 164) proved that gaseous mixtures capable of propagating the explosion-wave lost this property when certain proportions of nitrogen were added. The retarding effect of nitrogen on the propagation of flame has been demonstrated in the case of the explosion-wave by Dixon (*Phil. Trans.*, 1893, *A*, **184**, 165) and in the case of the "uniform movement" by Mason and Wheeler (J., 1917, **111**, 1048). The remaining type of inflammation, that from the closed end of a tube, remains to be considered.

Experiments in which varying percentages of fuel were burnt with an "atmosphere" of constant proportions gave curves similar in type to those for the "uniform movement" (Wheeler, J., 1914, **105**, 2608). An interesting result was obtained, however, when the fuel : oxygen ratio was kept constant and the nitrogen content varied. The factor of mass action being thus cut out, it was possible to study the speed variations due alone to progressive dilutions.

On plotting the speed results against the successive additions of nitrogen, the curve appeared essentially hyperbolic. The speeds were now plotted against calorific values, calculated by dividing the heat of combustion of the fuel by the total number of reacting and diluent molecules in the equation, the ratio fuel : oxygen being in every case that for complete mutual combustion. The curve produced was a straight line (Fig. 1).

Thus for any basic mixture subjected to successive nitrogen dilutions, the speed is directly proportional to the calorific value. This law ceases to hold good in the neighbourhood of the limit mixtures, but is true up to and beyond the proportions where the "atmosphere" is air. A simple algebraic exercise demonstrates that the speed–nitrogen curve must be an hyperbola of the form $x + xy + ay = k$.

There are no comparable data of the "uniform movement"; but in the case of the detonation wave, if the rates of explosion given by Dixon (*loc. cit.*) for the mixtures $2H_2 + O_2 + xN_2$ are plotted against the calorific values, the curve approximates very closely to a straight line (Fig. 2), only departing from it in the case of the most dilute mixture, where the velocity is slightly too low. The results for the mixtures $2CH_4 + 3O_2 + xN_2$, $C_2H_4 + 2O_2 +$

xN_2, and $2C_2H_2 + 3O_2 + xN_2$, given in the same paper, if plotted in a similar way, lie on a smooth curve which is no longer a straight line, but is in each case concave to the horizontal axis. Now were

FIG. 1.

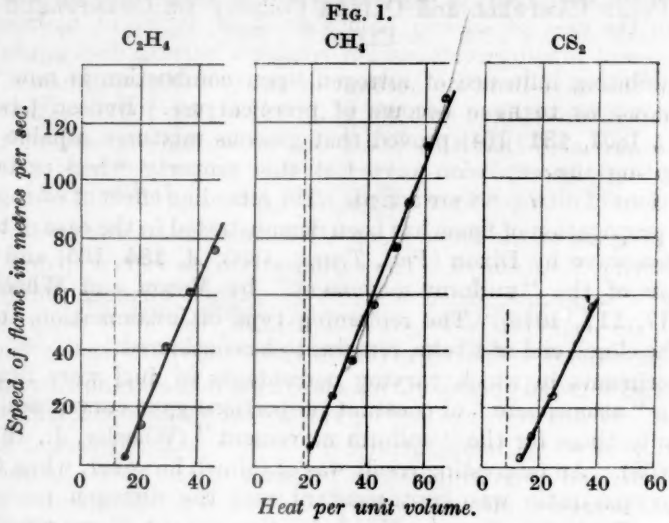
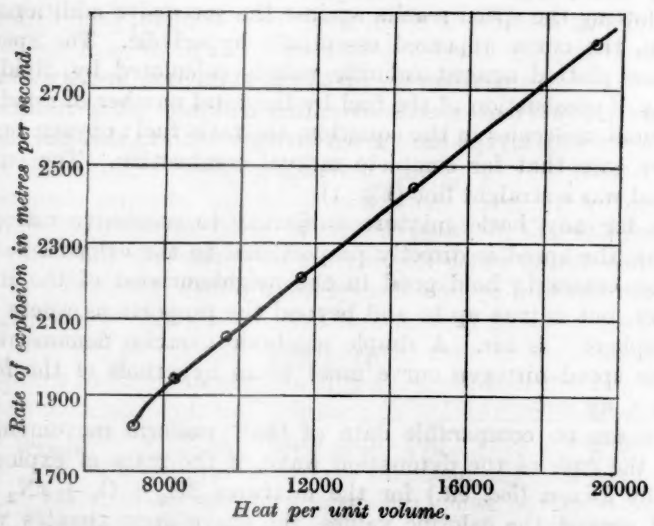


FIG. 2.



it a straight line, it would lead us to suppose that the suggested dependence of the speed on the calorific value is fallacious in the case of the detonation-wave, since in this case the combustion in

the head of the flame is incomplete, and its heat value, therefore, unknown; as it is curved, however, it leaves open the interesting possibility that the speed of the detonation-wave is also proportional to the heat value of the combustion in the head of the flame. Even in the case of carbon monoxide itself, sufficient hydrogen being present to induce combustion, complete burning does not take place in the wave-front on account of the $CO : CO_2$ equilibrium at this temperature (Dixon and Walls, J., 1923, **123**, 1031), so that it seems improbable that this point can be settled by any of the present methods.

EXPERIMENTAL.

The progress of the flame along a horizontal tube was measured by a moving-film camera. The earlier mixtures were prepared by passing a measured, dried amount of oxygen–nitrogen mixture through the appropriate weight of liquid fuel, the latter being thus added as vapour. The tripartite mixture was now passed backwards and forwards between two mercury gas-holders until homogeneous. Means were provided for keeping the gas-holder connexions and firing-tube at a temperature high enough to avoid partial condensations, and this temperature for some of the fuels—pentane, hexane, benzene, alcohol, ether, and carbon disulphide—was considerable.

It was found that the " initial phase " of inflammation endured for a minimum distance of 8 cm. from the spark-gap, even with the fastest mixtures, all of which detonated. The progress of the flame was therefore measured over the first 5 cm. of its path, and the speeds given are the average speeds over this distance. The results of experiments with all the fuels given above tended to the conclusion already stated, but there were anomalous cases; the authors were impressed by the great changes in speed due to slight changes in the construction of the tube, changes of initial temperature, changes in the time during which the mixture had been kept hot; this led to the examination by one of us (Ellis, J., 1923, **123**, 1435) of the influence of physical factors, and the investigation was repeated with gaseous fuels at room temperature. The size of the tube, the position and width of the spark-gap, and the intensity of the spark were maintained as constant as possible. All the experiments were performed in the same firing-tube, which was 83 cm. long and 1·95 cm. in diameter; the platinum electrodes were fused in at a point 13·2 cm. from the end; the distal end was opened just before ignition, thus eliminating another factor—the effect of the length of the tube—which varies with flames of different speeds; the spark was a discharge from a condenser of 0·000435 microfarad through a gap of 1 mm.

The curves are given for methane, ethylene, and carbon disulphide, the heat per unit volume in each case being calculated from the following heats of combustion: $CH_4 = 213{\cdot}3$ cal.; $C_2H_4 = 316{\cdot}2$ cal.; $CS_2 = 265$ cal. In each curve, the dotted line indicates the heat per unit volume of the "limit" mixture, this containing the maximum proportion of nitrogen which will permit the propagation of flame.

The authors warmly thank Mr. Sydney Robert Stubbs for valuable experimental assistance in this work.

THE VICTORIA UNIVERSITY OF MANCHESTER.

MINES DEPARTMENT EXPERIMENTAL STATION, SHEFFIELD.

[*Received, July 1st*, 1924.]

CCLII.—*The Influence of Nitrogen Dilution on the Speed of Flame. Part II.*

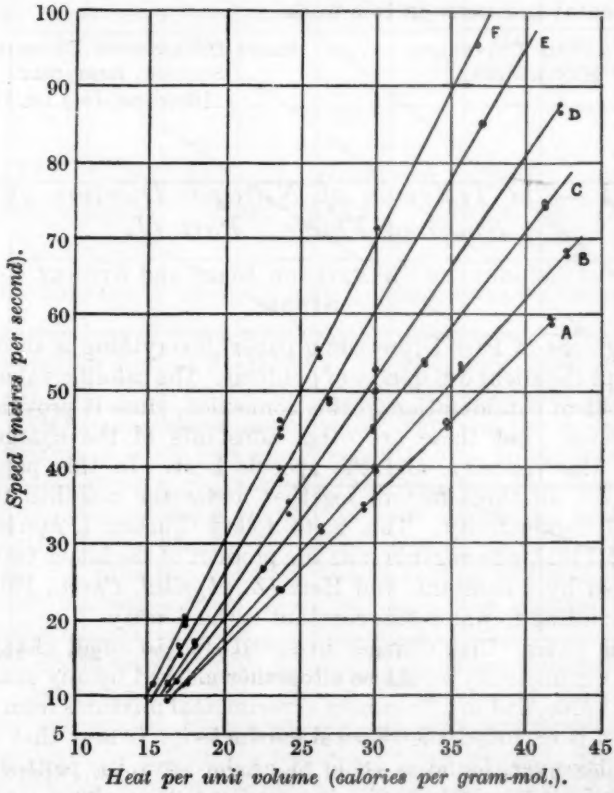
By OLIVER COLIGNY DE CHAMPFLEUR ELLIS and SYDNEY ROBERT STUBBS.

IN the graphs of Part I (preceding paper), everything is accounted for except the slight differences of gradient. The calorific value must be left out of consideration in this connexion, since it provides one of the axes; but there are other constants of the charge—the density, the viscosity, and the specific heat. In this paper we have taken all three factors together under the omnibus title of Thermal Conductivity. This is to follow Eucken (*Physikal. Z.*, 1911, **12**, 1101), who regards it as the product of the latter two data, multiplied by a constant, and Herz (*Z. physikal. Chem.*, 1919, **93**, 376), according to whom this constant is the density.

It was patent that changes in speed due to small changes in thermal conductivity would be altogether masked by any change in calorific value, and in all common experimental mixtures from which hydrogen is excluded the thermal conductivity is near that of air. It was, however, found possible to produce graphs, plotted as in Part I, of progressively increasing gradient, by making a number of mixtures of carbon disulphide and hydrogen together with the "theoretical" oxygen, and expanding each of these into a separate series of mixtures by additions of nitrogen. It was surprising to find that the gradients of these speed–calorific-value graphs (Fig. 1) were apparently proportional to the thermal conductivities of the basic mixtures; that is, a datum referring to a series of mixtures was proportional to another datum referring only to the first of them. This proved, however, to be merely a geometrical corollary of another

result: an analogous set of six straight lines was obtained by plotting speed against thermal conductivity, and a third set by plotting thermal conductivity against heat per unit volume. From these curves, it was now possible to read off the speeds for mixtures differing in respect of thermal conductivity, but having the same (chosen) calorific value. It was found (Fig. 2) that when the calorific value is the same for a set of mixtures, the speeds of the

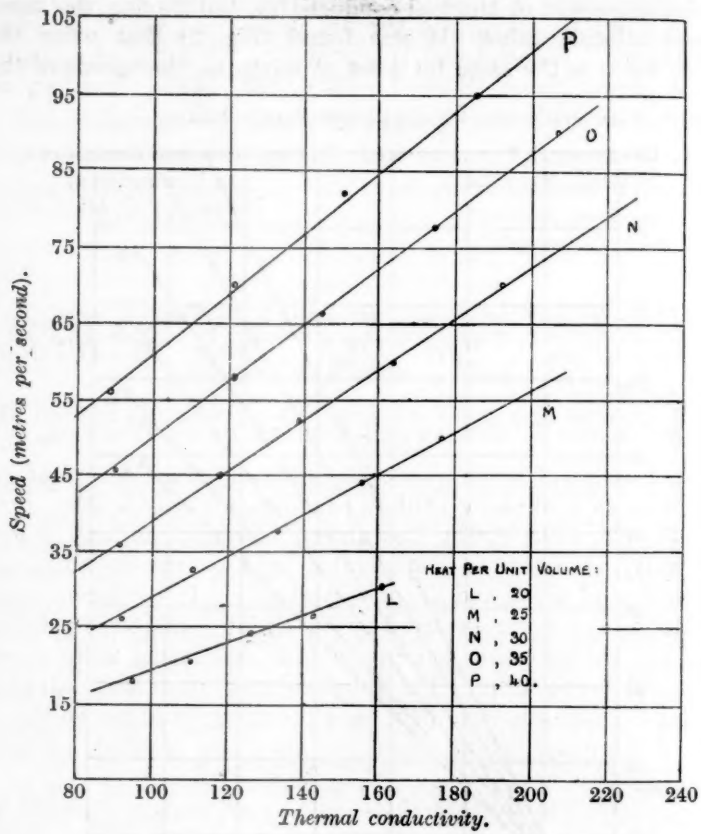
FIG. 1.



mixtures are directly proportional to their thermal conductivity. This conclusion is of high importance in that it provides a simple experimental means for the determination of the thermal conductivity of a gas whether combustible or inert. The special nature of the result is, of course, recognised. Even the fuel is changed in the course of the experiments, the carbon disulphide varying from 25 to 13·9 per cent. of the basic mixture, and the hydrogen from 0 to 29·2 per cent. A wider scope will therefore

be sought for this generalisation; the experiments will be repeated with the "uniform movement" and if there is a parallelism of result, the work will be continued with this type of inflammation.

FIG. 2.



EXPERIMENTAL.

The basic mixtures were all of the form $xC + yE$, where $C = CS_2 + 3O_2$ and $E = 2H_2 + O_2$. In order to obtain wide variations of thermal conductivity, the following basic mixtures were employed:

	Thermal condy.	x.	y.		Thermal condy.	x.	y.
A	82	100	0	D	200	303	: 118
B	100	403	: 18	E	250	253	: 168
C	150	353	: 68	F	300	203	: 218

The thermal conductivities of the mixtures were calculated by alligation from those of the constituents: hydrogen 704, oxygen 100,

nitrogen 100, carbon disulphide 28. Conversely, the proportions of the constituents were calculated to give any desired thermal conductivity.

The experiments were carried out as described in Part I, except that, in order to exaggerate the differences in gradient, a weak "jump-spark" was employed, this producing, for any given mixture, a much slower flame (Ellis, J., 1923, **123**, 1435). Further, all mixtures were made and fired at room temperature.

MINES DEPARTMENT EXPERIMENTAL STATION, SHEFFIELD.

THE VICTORIA UNIVERSITY OF MANCHESTER.

[*Received, July 1st*, 1924.]

CCLIII.—*Researches on Residual Affinity and Co-ordination. Part XXI. Boron β-Diketone Difluorides.*

By GILBERT T. MORGAN and RICHARD BRIAN TUNSTALL.

THE interactions of boron trichloride or silicon tetrachloride and the β-diketones as studied by Dilthèy (*Annalen*, 1905, **344**, 300; *Ber.*, 1903, **36**, 923, 1595, 3207; Rosenheim, Löwenstamm, and Singer, *ibid.*, 1834) have thrown considerable light on the co-ordination relationships of boron and silicon respectively. In the former case, two chlorine atoms were replaced by two chelate β-diketonic radicals, giving the characteristic number of four associating units round the central boron atom. The third chlorine atom was extruded from the co-ordination complex, thus becoming ionisable, so that a series of bisacetylacetone boronium salts was isolated, such as $[(C_5H_7O_2)_2B]AuCl_4$ or $FeCl_4$; $[(C_5H_7O_2)_2B]_2PtCl_6$.

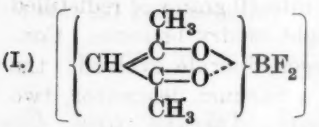
With silicon tetrachloride, three chlorine atoms were replaced by three chelate β-diketonic groups. The central silicon atom became surrounded by six associating units corresponding with the maximum co-ordination number for this element, whereas the fourth chlorine atom was rendered ionisable by extrusion from the co-ordination complex, thus giving rise to the structure $[Ac_3Si]Cl$, from which such double siliconium salts as the following were obtained :—trisacetylacetone siliconium salts, $[(C_5H_7O_2)_3Si]I$, $[(C_5H_7O_2)_3Si]_2PtCl_6$; trisbenzoylacetone siliconium salts,

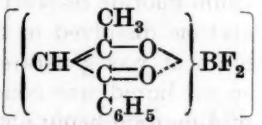
$[Benzac_3Si]FeCl_4$ or $AuCl_4$;

trisdibenzoylmethane siliconium salts, $[Dibenz_3Si]_2ZnCl_4$ and $[Dibenz_3Si]SnCl_5$. These results are, however, contingent on the use of the chlorides of boron and silicon, for when the corresponding fluorides are employed the phenomena observed are quite different.

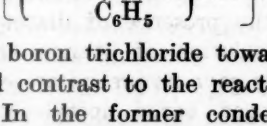
Silicon tetrafluoride is entirely inert towards the β-diketones and no rise of temperature is discerned on passing excess of the gas into concentrated anhydrous solutions of these organic substances.

Boron trifluoride, on the contrary, reacts energetically with β-diketones, considerable heat being generated. When passed into a strong benzene solution of acetylacetone, this gas is absorbed and hydrogen fluoride is liberated. On concentrating the warm solution, *boron acetylacetone difluoride* separates as a very soluble, crystalline product having the monomeric structure denoted by formula I.

(I.) 

 (II.)

When boron trifluoride is passed into an anhydrous solution of benzoylacetone, *boron benzoylacetone difluoride* is deposited as a well-defined, colourless, crystalline compound also possessing the physical and chemical properties of a monomeric substance (formula II). Neither of these substances shows indication of the presence of the borofluoride radical. A similar result was obtained in the case of dibenzoylmethane, except that the product, *boron dibenzoylmethane difluoride* (III) was yellow and very sparingly soluble.

 (III.)

The behaviour of boron trichloride towards β-diketones stands evidently in marked contrast to the reactions now studied with boron trifluoride. In the former condensation, examined by Dilthey and others, two-thirds of the halogen are replaced by β-diketonic groups and an ionisable product results. But in the present instance, substitution of only one fluorine atom by the chelate group takes place, so that in these *boron β-diketone difluorides* the co-ordination number, four, is made up of two units derived from the β-diketonic radical and two units of fluorine. The latter thus remain within the complex and are entirely non-ionised.

Experimental.

Boron acetylacetone difluoride (formula I), large, colourless plates from chloroform–ligroin, m. p. 43°: very soluble in benzene, decomposed by warm alcohol, almost insoluble in light petroleum:— 0·1207 gave 0·1799 CO_2, 0·0531 H_2O; C = 40·21, H = 4·89. 0·2483

gave 0·1324 CaF_2; F = 25·9. 0·1524 gave 0·0647 $B(OH)_3$; B = 7·54. *M* (by cryoscopy in benzene, *c* = 0·61) = 181. $C_5H_7O_2F_2B$ requires C = 40·54; H = 4·73; F = 25·66; B = 7·43 per cent.; M (for monomeride) = 148.

Preparation :—Boron trioxide (10 gms.) was dissolved by warming in 67 c.c. of sulphuric acid (*d* = 1·83) and, after cooling, 20 gms. of calcium fluoride were added and the solution gradually heated, any silicon tetrafluoride evolved below 140° being allowed to escape. The boron trifluoride evolved above this temperature passed through three bottles (one empty and the others containing boron trioxide and sodium fluoride respectively), thence into 10 grams of redistilled acetylacetone dissolved in the same weight of dry benzene. Considerable heat was generated and hydrogen fluoride evolved; the deep brown liquid was concentrated in a vacuum desiccator, two crops of difluoride being obtained.

Chemical Properties of Boron Acetylacetone Difluoride.—The crude product is decomposed by moist air with production of hydrogen fluoride and acetylacetone, but is moderately stable when purified. Heated in a dry tube, it decomposes with evolution of acetylacetone and acid fumes giving the boron flame coloration, and with formation of a crystalline sublimate, probably boric acid. It is hydrolysed by dilute hydrochloric acid, liberating acetylacetone. Strong aqueous ammonia and calcium nitrate gave a flocculent precipitate of calcium fluoride. Tests for the presence of the borofluoride radical, BF_4, were fruitless. Alcoholic potassium iodide gave no potassium borofluoride and alcoholic potash produced a gelatinous precipitate giving the reactions of fluoride and borate. No evidence could be obtained of the presence of diacetylacetone-boronium, $[BAc_2]'$, a chloroform solution of lithium chloride followed by anhydrous ferric chloride gave no precipitate even on adding light petroleum, and unchanged boron acetylacetone difluoride was recovered by benzene extraction from the solid residue of the chloroform solution.

Boron benzoylacetone difluoride (formula II), long, transparent, colourless, highly refractive prisms from benzene, rhombohedra from chloroform, m. p. 155° :—0·0918 gave 0·1923 CO_2, 0·0365 H_2O; C = 57·06, H = 4·42. 0·5400 gave 0·2030 CaF_2; F = 18·34. 0·1998 gave 0·0572 $B(OH)_3$; B = 5·11. *M* (ebullioscopy in benzene, *c* = 1·73) = 229. $C_{10}H_9O_2F_2B$ requires C = 57·15; H = 4·29; F = 18·23; B = 5·24 per cent.; *M* (monomeride) = 210.

Preparation :—Boron trifluoride was passed into a concentrated solution of recrystallised benzoylacetone in dry benzene containing a little light petroleum, the colourless crystalline product was separated from benzene or chloroform at various temperatures;

individual crystals were tested by melting-points for isomeric forms, but only one compound was obtained.

Boron dibenzoylmethane difluoride (formula III), yellow, crystalline needles from hot chloroform, m. p. 191°, very slightly soluble in benzene, insoluble in light petroleum :—0·0868 gave 0·2093 CO_2, 0·0346 H_2O; C = 65·74, H = 4·43. 0·4967 gave 0·1453 CaF_2; F = 14·24; 0·3012 gave 0·0645 $B(OH)_3$; B = 3·80. *M* (cryoscopy in naphthalene, *c* = 2·94) = 271. $C_{13}H_{11}O_2F_2B$ requires C = 66·1; H = 4·04; F = 13·97; B = 4·04 per cent.; *M* (monomeride) = 272.

Preparation :—Boron trifluoride was passed into a benzene solution of dibenzoylmethane at 0°, heat generation being very appreciable. The yield of copious yellow, crystalline precipitate was quantitative.

When either of the three foregoing boron β-diketone difluorides is dissolved in glacial acetic acid, there is no appreciable change in the electrical conductivity of the solvent.

Methods of Analysis.—Owing to the presence of both boron and fluorine in the foregoing co-ordination compounds, analytical difficulties arose and were surmounted as follows :—(1) The combustion tubes for carbon and hydrogen were packed with a mixture of lead chromate and granular copper oxide followed by a roll of ignited asbestos paper containing 10 cm. of lead dioxide gently warmed (below 400°) to trap volatile fluorine and boron compounds. The weighed substance was mixed in the boat with twice its weight of powdered copper oxide.

(2) For fluorine estimations, the weighed substance was boiled with 10 c.c. of 30 per cent. potassium hydroxide until the diketone was completely hydrolysed, water added to maintain the original volume, and 5 grams of solid ammonium nitrate were introduced followed by 200 c.c. of boiling water and 0·5 to 1 gram of calcium nitrate, the solution being boiled for 5 minutes. After 1 hour on the water-bath, the precipitate was collected, washed with 0·1 per cent. acetic acid, dried, and ignited in a weighed crucible, the filter-paper being incinerated separately. The precipitates from the acetylacetone and benzoylacetone derivatives can be ignited and weighed as CaF_2 without further treatment. The dibenzoylmethane compound yielded a product containing calcium benzoate, and after ignition to convert this to carbonate the residue was evaporated twice to dryness on the water-bath with 1 c.c. of glacial acetic acid. The crucible contents were extracted with boiling water to remove calcium acetate and the residual calcium fluoride was ignited and weighed.

(3) Boron estimation :—An adaptation of the method by I. C.

Jones (*Amer. J. Sci.*, 1899, [iv], **7**, 147). The weighed boron β-diketone difluoride was completely hydrolysed with aqueous potassium hydroxide, and the solution filtered if necessary and made up to definite volume; 25 c.c., which should contain less than 0·1 gram of boric acid, were made slightly acid to litmus with hydrochloric acid and treated with 10 c.c. of 10 per cent. barium chloride to precipitate fluoride and carbonate. Ten c.c. of 25 per cent. potassium iodide and 10 c.c. of saturated sodium iodate were added and the liberated iodine was removed by strong aqueous sodium thiosulphate, using starch as indicator. After testing the liquid for neutrality with iodate–iodide mixture, a few drops of phenolphthalein were added and *N*/10-sodium hydroxide was run in until a pink colour developed. Two grams of mannitol were added and the alkali titration of the decolorised solution was continued until the colour returned. If this coloration persisted on adding more mannitol, the second titration was taken as the correct reading.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research for grants which have helped to defray the expense of this investigation.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

[*Received, July 4th*, 1924.]

NOTES.

Conversion of Nickel Carbonyl into Carbonate in Toluene Solution.

By PERCY CYRIL LESLEY THORNE.

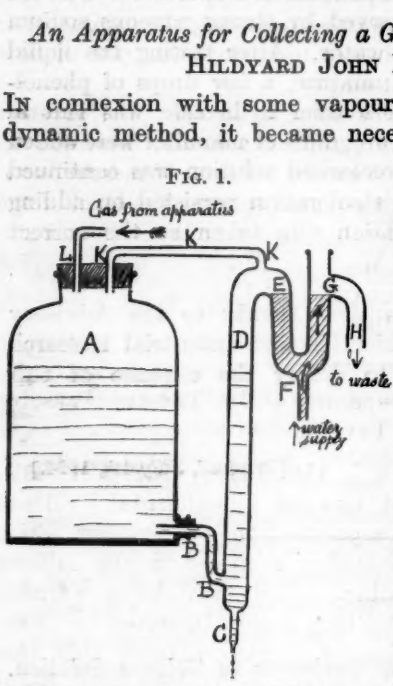
A DISTURBING feature of some work on the formation of colloidal solutions of nickel in toluene by the decomposition of nickel carbonyl (Hatschek and Thorne, *Proc. Roy. Soc.*, 1923, **103**, [*A*], **276**; *Kolloid-Z.*, 1923, **33**, 1) was the formation of a gelatinous, green precipitate when even small quantities of air had access to the solution. The precipitate formed rapidly when the stock solutions of nickel carbonyl used in the main investigation were exposed to the air. When these solutions were thereby rendered too weak to be of use for the preparation of the colloidal solutions, the precipitate was filtered off and air-dried (Found: Ni = 39·63, 40·11; CO_2 = 15·92, 16·21 per cent.). It lost water (22·53 per cent.) at 120° and became yellow, and was converted into black nickel oxide on ignition.

No gas other than carbon dioxide was evolved on decomposition with dilute hydrochloric acid. The substance would therefore appear to be a basic carbonate of nickel (compare Mond, *J. Soc. Chem. Ind.*, 1892, **11**, 750), and not a compound of carbonyl and hydroxide, $Ni(CO)_4,2Ni(OH)_2,4H_2O$, as suggested by Lenher and Loose (*J. Amer. Chem. Soc.*, 1900, **22**, 114).—The Sir John Cass Technical Institute, Jewry St., Aldgate. [*Received, May 7th*, 1924.]

An Apparatus for Collecting a Gas at a Constant Pressure. By Hildyard John Eglinton Dobson.

In connexion with some vapour pressure measurements by the dynamic method, it became necessary to collect 10—15 litres of gas over a period of several hours, at a constant (atmospheric) pressure. The gas was collected in an aspirator by displacement of water, and in order that the gas should be continuously at atmospheric pressure, the rate of outflow of water had to be regulated constantly in order to keep it equal to the rate of inflow of gas from the vapour pressure apparatus. The following automatic pressure regulator, devised for this purpose, depends on the provision of an external supply of water which automatically overflows into the aspirator as soon as the pressure in it falls below atmospheric, and ensures that the *net* outflow of water is always equal to the inflow of gas.

Fig. 1.



It is found most convenient to cause water to flow, not into the aspirator, *A*, itself, but into the wide side tube, *D*, connected to the top and bottom of the aspirator through the tubes *KK* and *BB* respectively, its lower end, *C*, serving also as the water outlet from the aspirator.

The essential feature of the apparatus is the U-tube *EFG*; tap water (from an air-trap if necessary) enters at *F*, and maintains a constant level in the open tube at *G*, flowing to waste through the tube *H*. The limb, *E*, connects with the tube *D* at the same level as *G*, and consequently water will overflow in large quantities into *D* as soon as the pressure in the aspirator becomes less than atmo-

spheric. The result of this overflow of water into *D* is the same as if water had been added directly to the aspirator, *viz.*, the pressure in the aspirator rises until it is again atmospheric, when the overflow of water automatically ceases. The existence of a pressure in the aspirator greater than atmospheric is prevented by making the outlet, *C*, sufficiently wide to allow water to flow freely under its own weight from the aspirator, more rapidly than the gas enters through the tube *L* from the experimental apparatus. For this reason the tube *BB* is bent downwards on leaving the aspirator, so that there is sufficient height of water to ensure this rate of flow even when the aspirator is almost empty.

This apparatus has proved very efficient in use; the greatest deviation from barometric pressure during 5 hours, in which 15 litres of gas were collected, did not exceed 0·1 mm. of mercury.

For working at pressures other than atmospheric, the level of the outflow, *G*, could be made considerably higher or lower than *E*.

The author's thanks are due to Mr. G. A. Elliott for many helpful suggestions.—The Ramsay Laboratories, University College, London. [*Received, May 22nd,* 1924.]

Solid Phases of Invariable Composition. By Thomas Weston Johns Taylor.

Rivett and Clendinnen (J., 1921, **119**, 1329; 1922, **121**, 801; 1923, **123**, 1634) have brought forward experimental evidence that certain solid phases which separate from the systems which they have studied are not, as heretofore supposed, double salts of invariable composition, but rather mixed crystals of variable composition. In addition to this, they have attempted to prove from the basis of the second law of thermodynamics that this must always be the case, and that every such phase must be of variable composition, although the limits of possible variation may be small.

This conclusion is quite possibly correct; but the two attempted thermodynamical proofs advanced by these authors can be shown to be unsound, and it is suggested that no such general proof can be obtained from the sole use of the second law.

One argument they have used (J., 1923, **123**, 1639) rests on the assumption that if two phases can each be in equilibrium with a third, they must necessarily be able to exist in equilibrium with each other. This assumption is unjustifiable (compare Gibbs, "Collected Papers," Vol. I, p. 62 *et seq.*). For if two phases *A* and *B* can each be in equilibrium with a third phase *C*, which does not contain a substance present in *A* and *B*, then for equilibrium

between A and C the chemical potential of that substance in A need not bear any particular relationship to the chemical potential of the substance in C, other than not being greater than it; and similarly for the potentials of the substance in the equilibrium B–C. So that if A and B are placed in contact, equilibrium need not exist, since the substance is present in A and B, but its chemical potential is not necessarily equal in the two phases.

Their other argument will be found in J., 1921, **119**, 1337: a two-component system in two phases with the vapour phase absent is considered; by the phase rule the system is univariant; it is argued that if one phase is such that its composition can remain unchanged in contact with the other phase over a small range of temperature, then defining the composition of this phase does not completely define all the variables of the system, as the authors appear to consider it should, and hence, since the phase rule is true, the case is impossible. The error in this argument will appear in the following: such a system has five variables, temperature and four concentration terms, the concentrations of each of the components in each of the phases. In general, there are four equations to be satisfied for equilibrium, the two chemical potential equations for the components and the two equations of state for the phases; thus the system is univariant. If one phase is a pure component, one chemical potential equation disappears (compare *supra*) and one concentration term disappears; hence the system can still be said to be univariant. But this concentration term which has disappeared no longer counts as a variable, in the sense that if a value be assigned to it, we are still left with four unknowns and three equations. If, however, a value be assigned to any one of the other concentration terms or to the temperature, these are variables and the system is completely defined; it is well to remember that the terms are concentrations and not compositions. In the argument cited above, a value is assigned to a term which is not a variable within the meaning of the phase rule.

It will be noticed that if, in addition to the second law, we assume that every substance is soluble to some extent in every phase, then both the above arguments would be true, because the cases where they break down would be impossible. This assumption, however, is not implied in the second law, and if it were true, the arguments would obviously be unnecessary. But it may be doubted if it is universally true; a closely packed crystal such as the diamond may be completely impermeable by a substance consisting of large molecules.—BRASENOSE COLLEGE, OXFORD. [*Received, May 12th,* 1924.]